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XX.—ON PALMITIC ACID AND THE PALMITINS.

BY R. H. CHITTENDEN AND HERBERT E. SMITH.

In an attempt to prepare synthetically a palmityl lecithin we have been led, as a preliminary step, to a study of palmitic acid and its glycerin compounds. In the literature of the subject we have found but comparatively few concise statements concerning these bodies, and those frequently contradictory to the results of our experiments, particularly in regard to the synthetical preparation of the three palmitins. Detailed knowledge of these bodies, of the methods to be used in their preparation, and how to accurately determine the content of palmitic acid in these and other compounds containing the palmitic acid radical, was essential to the success of our work. We have, therefore, made a thorough study of these points; and the results, some of which are new and others simply confirmatory of previous discoveries, we present here as an aid to future workers in the same field.

Preparation of Palmitic Acid.

The difficulty of preparing palmitic acid perfectly pure, that is, entirely free from adhering traces of stearic or other acids not differing greatly in solubility, with which the former is so intimately associated in many of both the animal and vegetable fats, has been clearly shown by the laborious work of Heintz.[1] It therefore

[1] Journal für prakt. Chem. **66**, 1. Poggendorf's Annalen **92**, 429. Watt's Dict. of Chem. **3**, 1070.

seemed desirable to use such material as would be most likely to yield the acid at the outset in the purest condition and with the least labor. All of the more common sources of palmitic acid, as palm oil, contain the troublesome olein. The Chinese vegetable tallow from the *Stillingia sebifera*, so thoroughly studied by Maskelyne,[1] while a good source of palmitic acid, likewise contains the objectionable olein. The wax of the *Myrica cerifera* or bayberry tallow, a commercial article easily obtainable, has been shown by Moore[2] to consist of "about *one-fifth* part of *palmitin*, the remaining *four-fifths* being free palmitic acid with a small quantity of lauric acid, the latter either free or in the state of *laurin*." The latter is present in such small quantity and differs so widely from palmitic acid in solubility, melting point and composition, that it would seem as if no better source of the acid could possibly be obtained. We have, therefore, employed this article in the preparation of the pure acid.

Several pounds of the commercial tallow were saponified with sodium hydroxide, and on cooling the concentrated solution the sodium salts of the two fatty acids floated as a granular mass on the surface of the fluid, separating from the strong lye in the same manner as from a concentrated salt solution. This mass was skimmed off, dissolved in hot water, filtered, and the solution then acidified with dilute sulphuric acid. When cold the palmitic acid, with probably some lauric, was removed as a solid crust. It was then freed from sulphates by thorough washing with hot and cold water, after which it was dissolved in hot 95 per cent. alcohol, filtered while still hot through animal charcoal and then allowed to crystallise by simple cooling. The crystals so obtained were purified by repeated crystallisations from hot alcohol. The comparatively easy solubility of lauric acid in cold alcohol would seem to guarantee its complete separation by one or two crystallisations.

Two distinct preparations of palmitic acid were obtained from the final crystallisation:

A, being the product crystallising from the alcohol by simple cooling.

B, a second crop of crystals obtained by concentrating the filtrate from A.

The solubility of palmitic acid in cold alcohol is greater than

[1] Quart. Jour. Chem. Soc. **8**, 1. [2] Amer. Jour. Sci. and Arts, 2d Ser., **33**, 313.

would at first appear. Thus we found by experiment that in 100 parts of absolute alcohol (sp. gr. 0.787 at 22° C.) there were dissolved in 24 hours at 19.5° C. 9.209 parts of the acid. When warmed with the absolute alcohol until completely dissolved and then allowed to stand for 24 hours at 19.5° C. there were dissolved (in 100 parts) 9.428 parts of the acid.

Composition of A.

I. 0.2562 gram gave 0.2877 gram H_2O and 0.7001 gram CO_2.
II. 0.2507 gram gave 0.6883 gram CO_2.
III. 0.2826 gram gave 0.3228 gram H_2O and 0.7720 gram CO_2.

Composition of B.

IV. 0.3388 gram gave 0.3818 gram H_2O and 0.9315 gram CO_2.
V. 0.3604 gram gave 0.9872 gram CO_2.

	A.			B.		Theory.	
	I.	II.	III.	IV.	V.	Palmitic acid.	Lauric acid.
C	74.54	74.88	74.50	75.00	74.71	75.00	72.00
H	12.48		12.69	12.53		12.50	12.00
O	12.98		12.81	12.47		12.50	16.00

It is thus evident that in composition the acid was quite pure. The melting point of the acid, determined in a thin-walled capillary tube, was as follows:

	A.	*B.*
(*a*)	melted at 61.50° C. and solidified at 59.50° C.	Melted at 61.9° C.
(*b*)	" 62.05° C. " 60.05° C.	

According to Heintz, pure palmitic acid melts at 62° C.
With this acid all of the following experiments were tried.

Quantitative Determination of Palmitic Acid.

Noticeable variations in the methods of determining this acid as given by different authorities would seem to demand some explanation. It is quite evident from our results that while the variations noticed are not great in themselves, on them hinge mainly the accuracy or inaccuracy of the method. We are not concerned here with the separation of palmitic acid from its closely allied neighbor, stearic acid. Fractional precipitation by means of barium and lead salts has always been deemed sufficient to accomplish this, not

only from this one acid, but also from the other fatty acids with which palmitic is frequently associated. Well-defined statements, supported by experimental data, bearing on the precipitation of palmitic acid as a barium or lead salt, we have, however, been unable to find. One would infer from the literature of the subject that such precipitations are complete. It is without doubt true that complete separation of the acid as a barium or lead salt can be effected, but not, we believe, always in a manner suitable for its accurate quantitative determination.

There are apparently in general use two ways of precipitating palmitic acid: 1st, by simply adding a solution of barium chloride, lead acetate or calcium chloride either in water or alcohol to a hot alcoholic solution of the free acid; 2d, by addition of the precipitant to an alcoholic solution of an alkaline salt of the acid. Judging from some descriptions[1] of methods it would appear that this latter point can be most conveniently accomplished by the simple addition of ammonium hydroxide to the boiling alcoholic solution of the free acid until the former is present in slight excess. Addition of the reagent is then followed by precipitation of the acid in combination with the base added. The reasons why precipitations made by either of these methods are liable to give very poor results are to be found in the decomposition of both barium and lead palmitates by water, also by alcohol containing acetic acid, yet washing of the barium palmitate precipitate by water is quite necessary when even a slight excess only of an aqueous solution of barium chloride is added to either an alcoholic or an ammoniacal alcoholic solution. Equally necessary is it to wash the same precipitate with alcohol containing a little acetic acid when previous to precipitation the free fatty acid has been converted into a sodium palmitate by boiling with sodium carbonate, for under such circumstances a trace of sodium carbonate is liable to dissolve in the boiling absolute alcohol used to separate it and thus form barium carbonate. Again, we have found that precipitation of palmitic acid from a hot alcoholic solution by an alcoholic solution of lead acetate, the mixture being allowed to stand in the cold for some time, invariably yields low results, not alone due to the solubility of the lead palmitate in alcohol, but apparently to the decomposing action of the acetic acid liberated by the reaction itself, yet ammonia added even in very small quantity gives a precipitate of lead hydroxide.

[1] Compare Maskelyne. Jour. Chem. Soc. **8**, 8–9.

All of our determinations of palmitic acid by precipitation with either barium chloride, acetate or lead acetate, followed by ignition and weighing as either barium sulphate or lead oxide, have invariably given us low results, and that in whatever way the precipitation was made. In no case, working with pure palmitic acid, have we succeeded in recovering more than 96 per cent. of the acid.

In Storer's Dictionary of Solubilities only indefinite statements are to be found concerning the palmitates, and we have thus been led to determine the solubility of several of the more insoluble salts of palmitic acid, as well as the action of dilute acetic acid on them. The purity of each salt experimented with was determined by analysis.

Calcium palmitate.

Ca calculated, 7.25 per cent.; Ca found, 7.14 per cent.

Solubility of the dry salt.—In 100 parts[1] of absolute alcohol (sp. gr. = 0.787 at 22° C.) there was dissolved in 22 hours at 20° C. 0.0103 part of the salt.

Barium palmitate.

Ba calculated, 21.17 per cent. Ba found, 21.19 per cent.

Solubility of the dry salt.—(*a*) In 100 parts of absolute alcohol there was dissolved in 22 hours at 20° C. 0.0035 part of the salt.

(*b*) In 100 parts of boiling[2] absolute alcohol there was dissolved in 6 hours 0.0128 part of the salt.

Solubility of the moist, freshly precipitated salt.—(*a*) In 100 parts of absolute alcohol there was dissolved in 24 hours at 21° C. 0.0146 part of the salt.

(*b*) In 100 parts of boiling absolute alcohol there was dissolved in 6 hours 0.0197 part of the salt.

(*c*) In 100 parts of absolute alcohol, containing 10 drops of acetic acid of sp. gr. 1.051, there was dissolved in 22 hours at 20° C. 0.0334 part of the salt.

(*d*) In 100 parts of boiling absolute alcohol, containing 10 drops of acetic acid of sp. gr. 1.051, there was dissolved in 6 hours 0.1486 part of the salt.

Magnesium palmitate.

Mg calculated, 4.49 per cent. Mg found, 4.58 per cent.

Solubility of the dry, crystallised salt.—(*a*) In 100 parts of absolute alcohol there was dissolved in 22 hours at 20° C. 0.0993 part of the salt.

[1] 1 part = 1 gram. [2] Evaporation prevented by inverted condenser.

(*b*) Warmed with absolute alcohol until completely dissolved, and then allowed to stand at 20.5° C. for 24 hours, there was dissolved in 100 parts 0.4869 part of the salt.

Lead palmitate.

Pb calculated, 28.87 per cent. Pb found, 28.45 per cent.

Solubility of the non-crystalline dry salt.—(*a*) In 100 parts of absolute alcohol there was dissolved in 24 hours at 19° C. 0.0007 part of the salt.

(*b*) Warmed with absolute alcohol until considerable had dissolved, and then allowed to stand for 24 hours at 19° C., there was dissolved in 100 parts 0.0027 part of the salt.

Solubility of the freshly precipitated crystalline salt.—(*a*) In 100 parts of absolute alcohol there was dissolved in 24 hours at 21° C. 0.0033 part of the salt.

(*b*) Warmed with absolute alcohol, whereby nearly all of the salt was dissolved and then allowed to stand at 21° C. for 24 hours, there was dissolved in 100 parts 0.0157 part of the salt.

(*c*) In 100 parts of absolute alcohol containing 10 drops of acetic acid, sp. gr. 1.051, there was dissolved in 24 hours at 21° C. 0.0391 part of the salt.

It is hence apparent that in alcohol alone, all of the salts experimented with are somewhat soluble, enough in many cases at least to interfere materially with an accurate determination of the acid. But the greatest source of error is to be found in the solvent action of any free acid present in the mixture. This is plainly shown in the action of acetic acid on both the lead and barium salts. It is, moreover, easily demonstrable that the action of the acid is a decomposing one, breaking up the salt with liberation of the fatty acid. Again, the decomposing action of water is liable to prove an important factor. The action of water on the alkali salts of this acid has long been known,[1] but apparently it has not been, at least generally, considered that the other salts were so affected; thus Maskelyne[2] directs, in the preparation of the barium salt, that it be washed thoroughly with water. The decomposition, however, takes place very readily, and is easily demonstrated by the fact that the water, either hot or cold, used in washing such a precipitate never ceases to contain either lead or barium, while hot alcohol

[1] Watt's Dictionary of Chemistry **4**, 334. [2] Journal Chem. Soc. **8**, 8-9.

poured over the precipitate so washed, deposits palmitic acid on cooling. The alternate solvent action of the water and alcohol, moreover, continues as long as any of the precipitate remains.

The method which we have finally adopted as the simplest and most accurate for determining palmitic acid, when in combination with glycerin or similar organic bases, is as follows: The first step is naturally a process of saponification. This is accomplished most advantageously by dissolving a weighed portion of the palmityl-containing substance in a small quantity of warm absolute alcohol in a capacious silver crucible, then adding an alcoholic solution of pure potassium hydroxide, and heating the mixture on a water-bath. After boiling gently for a short time the solution is evaporated to dryness. The residue is then dissolved in a little warm water, the solution diluted to 200–250 cc., after which the potassium palmitate is decomposed by the addition of hydrochloric acid. In this manner the acid is precipitated in large white flocks, if the solution was suitably cooled. The mixture is then heated to boiling, the melted acid floating on the surface of the fluid. After standing 24 hours the acid is filtered, washed with water until no further chlorine reaction can be obtained, then dissolved in a little boiling absolute alcohol, and the solution collected in a weighed glass bottle provided with a tightly fitting glass stopper. By evaporation of the alcohol the weight of the acid is easily obtained.

This simple method, which has in it nothing essentially new, has proved by far the most satisfactory of any that we have tried, and certainly there can be no possible fallacy connected with it. Theoretically a small amount of palmitic ether might possibly be formed by evaporation of the alcoholic solution of the acid, but if any is formed it is apparently in too small quantity to materially affect the result. Care, however, must be taken not to dry the palmitic acid residue for too long a time, as oxidation is liable to occur.

Following are some trial experiments with pure palmitic acid:

I. 1.0387 grams yielded after saponification 1.0407 grams acid = 100.19 per cent.

II. 0.4586 gram yielded after saponification 0.4578 gram acid = 99.82 per cent.

III. 0.3218 gram yielded after saponification 0.3234 gram acid = 100.49 per cent.

IV. 0.3807 gram yielded after saponification 0.3812 gram acid = 100.10 per cent.

V. 0.3782 gram yielded after saponification 0.3779 gram acid = 99.92 per cent.

VI. 0.4028 gram yielded after saponification 0.4007 gram acid = 99.47 per cent.

VII. 0.4266 gram yielded after saponification 0.4262 gram acid = 99.90 per cent.

VIII. 0.5518 gram yielded after saponification 0.5505 gram acid = 99.74 per cent.

Synthesis of the Palmitins.

Since Berthelot[1] announced the preparation of the three palmitins by synthesis, and the similarity of the artificially formed tripalmitin with the natural palmitin, but few additional experiments have been recorded confirming his results, or adding new data to those already acquired. By Berthelot's methods, all three of the palmitins can be prepared by simple heating of the free acid, with water-free glycerin for definite periods of time at definite temperatures; the latter, apparently, being more important than either the length of time or the proportion in which the acid and glycerin are mixed, for from Berthelot's description, this alone would appear to govern the production of the desired palmitin. According to the well-known statements[2] of Berthelot, *monopalmitin* melting at 58° C. and solidifying at 45° C. is formed by heating equal weights of glycerin and palmitic acid for 24 hours at 200° C., *dipalmitin* melting at 59° C. and solidifying at 51° C. by heating equal parts of glycerin and acid at 100° C. for 114 hours. It is likewise formed by heating a mixture of acid and glycerin 7 hours, at 275° C., while *tripalmitin* melting at 60° C. and solidifying at 46° C. is formed by heating monopalmitin for some hours with 10 to 15 times its weight of palmitic acid.

In spite of these definite statements, a large number of experiments lead us to the view that the formation of a *single* palmitin without admixture is rarely accomplished. Much more likely are we to obtain a mixture of all three in variable proportions, separable only by suitable solvents. This Hundeshagen apparently found to be the case in his recent synthetical preparation of the stearins,[3] particularly with the mono- and di-stearins. Moreover, the large

[1] Jahresbericht der Chemie **6**, 452-453; Journal für prakt. Chemie **58**, 412, and **60**, 193; Watt's Dict. of Chemistry **4**, 335; Chimie Organique **2**, 74-77.

[2] Chimie Organique **2**, 75.

[3] Journal für prakt. Chemie **28**, 224.

excess of glycerin, called for by Berthelot's process, would seem to interfere materially with the object in view, and indeed our own experiments have shown that much better results can be obtained by using the glycerin and palmitic acid in atomic proportions.

In an attempt to prepare monopalmitin by Berthelot's process, 100 grams of palmitic acid, and a like quantity of glycerin (Price's) previously rendered anhydrous by heating at 150°–180° C. for 4–5 hours, were heated for about 18 hours at 180–200° C. in a stoppered retort, the drawn-out end of which dipped under mercury. On being cooled the hardened fat was washed with water to remove adhering glycerin, and then warmed for a short time[1] with a small excess of calcium hydroxide to convert the free palmitic acid into a salt insoluble in ether. The fats freed from lime by washing with water, were dried in the air, and then extracted with warm ether, by the evaporation of which a residue of 51 grams of palmitins was obtained. According to Berthelot, this residue should consist of monopalmitin, since the method of preparation accords very nearly at least with his description. Tested, however, the crude product melted at 61–63° C., and began to solidify in fine crystals at 55° C. Analysis, moreover, showed that the dry product contained 91.38 per cent. of palmitic acid, plainly indicating that it was a mixture mainly of di- and tri-palmitin.

An attempt was then made to separate the palmitins by crystallisation from warm alcohol, a method which we have found quite convenient, as the three palmitins differ widely in solubility in this agent. The difference is even greater than we had at first supposed, as the following experiments made later with pure products clearly show.

Solubility of Tripalmitin.

Theoretical amount of palmitic acid in the substance, 95.28 per cent.; found, 95.26 per cent.

(*a*) In 100 parts of absolute alcohol (sp. gr. 0.787) there was dissolved in 2 hours at 21° C., 0.0053 part of the substance.

(*b*) Warmed with absolute alcohol until the fat was completely dissolved, then allowed to stand for 2 hours and filtered at 21° C., there was dissolved 0.0043 part of tripalmitin in 100 parts of alcohol.

[1] If heated for longer than 20–30 minutes, there is danger that considerable monopalmitin may be decomposed and the acid saponified.

Solubility of Dipalmitin.

Theoretical amount of palmitic acid in the substance, 90.14 per cent.; found, 90.14 per cent.

(*a*) In 100 parts of absolute alcohol there was dissolved in 2 hours at 20° C. 0.2097 part of the substance.

Raising the temperature a few degrees increases very greatly the solubility, thus at 27° C. there was dissolved in 2 hours 0.5040 part of dipalmitin in 100 parts of the absolute alcohol.

Solubility of Monopalmitin.

Theoretical amount of palmitic acid, 77.57 per cent.; found, 78.02 per cent.

(*a*) In 100 parts of absolute alcohol there were dissolved in 2 hours at 21° C. 4.1351 parts of the substance.

(*b*) Warmed with absolute alcohol until the fat was completely dissolved and then allowed to stand for 2 days at 22.5° C. there were dissolved in 100 parts of alcohol 5.3060 parts of monopalmitin.

Thus while tripalmitin is almost entirely insoluble in cold alcohol, dipalmitin is somewhat soluble and monopalmitin quite easily so. Again tripalmitin dissolves but slowly when warmed with alcohol, except when the latter is in large excess, and hence a mixture of these three bodies may be separated by simple treatment with hot and cold alcohol. Thus from the 51 grams of palmitins obtained by Berthelot's process, as described above, repeated crystallisations and re-crystallisations from alcohol yielded five products.

A, a portion of the fat which crystallised from slightly warm alcohol after the more insoluble tripalmitin had separated and before the more soluble monopalmitin had had a chance to crystallise; obtained constant after five crystallisations, melted at 70.5° C., solid at 66.5° C.

On analysis 1.2009 grams of the substance gave 1.0849 grams palmitic acid = 90.34 per cent. Evidently pure dipalmitin.

B, representing that portion of the palmitins which separated from the warm alcohol before *A*, but after the removal of the greater portion of the tripalmitin. This product made up the greater bulk of the yield, melted at 66.5° C., solid at 64.5° C.

On analysis 0.6286 gram gave 0.5790 gram palmitic acid = 92.10 per cent. This product we shall notice later on.

C, a product more soluble than *B*, obtained from the filtrates during the crystallisations of the latter, melted at 61° C., solid at 57° C.

On analysis (*a*) 0.3714 gram gave 0.3348 gram palmitic acid = 90.14 per cent.

(*b*) 0.4673 gram gave 0.4203 gram acid = 89.94 per cent. Also dipalmitin.

D, the most soluble portion of the palmitins, of which on analysis 0.7499 gram gave 0.6013 gram palmitic acid = 80.18 per cent. It thus approaches within 2.5 per cent. of monopalmitin, enough dipalmitin being mixed with it to raise the percentage.

E, representing the more difficultly soluble residues, melting at 63.5° C. and solidifying at 43° C.

On analysis (*a*) 0.9615 gram gave 0.9158 gram acid = 95.24 per cent.

(*b*) 0.4688 gram gave 0.4467 gram palmitic acid = 95.28 per cent. Hence the product was pure tripalmitin.

A second preparation of palmitins was made with the same amounts of palmitic acid and glycerin as before, but the mixture was heated at 180–200° C. for 45–50 hours. From the evaporation of the ether used in extracting the fats after saponifying with lime, there remained a residue which by treatment with alcohol (hot and cold) was resolved into three portions:

I. Soluble in a moderate bulk of cold alcohol.

II. A product more soluble than I, separating from the united filtrates only after further concentration.

III. An insoluble portion which separated even from a large quantity of alcohol. Little, if any, tripalmitin could be separated.

Products I and II contained respectively 78.70 per cent. and 79.57 per cent. of palmitic acid, thus approaching very nearly to monopalmitin. By recrystallisation of these two products a pure monopalmitin was obtained, melting at 63° C. and solidifying at 62.5° C.

Two analyses were made as follows:

(*a*) 0.8347 gram gave 0.6513 gram palmitic acid = 78.02 per cent.

(*b*) 0.7964 gram gave 0.6246 gram acid = 78.42 per cent.

Product No. III melted at 64.5° C. and solidified at 61° C.

Analysis showed 91.59 and 91.74 per cent. of palmitic acid. This, however, by repeated treatment with alcohol was resolved into two distinct and widely different portions:

A, a heavy crystalline precipitate separating from a large bulk of alcohol, melting at 69° C., solidifying at 62° C.

B, crystallising from the concentrated filtrate from A, melted at 49° C., solid at 48° C.

In the filtrate from *B* there were found traces of a body melting at 58° C. and solidifying at 50.5° C.,[1] also a body more insoluble, melting at 61–62° C. and solidifying at 53–54° C.

Product *B* was again crystallised from hot alcohol. The main bulk of the substance still retained the same melting point of 49° C., solidifying at 48° C. By the crystallisation, however, two small portions of fat were obtained, the more insoluble melting at 64.5° C., solidifying at 62° C., the other melting at 60° C. and solidifying at 52° C.

The body melting at 49° C. gave, on analysis, the following result:

0.4092 gram gave 0.3685 gram palmitic acid = 90.05 per cent.

In composition, then, this body would appear to be pure dipalmitin, although the melting point is much too low for the ordinary form; possibly this compound may represent an isomeric form of the fat.

Product *A* was recrystallised from warm alcohol, the main bulk of the substance retaining the melting point of 68.5°–69° C., but solidifying at 67.5° C. By this crystallisation a small insoluble residue (oily droplets) was obtained by dissolving in hot alcohol, which melted at 63.5° C. and solidified at 49–50° C.; probably mainly tripalmitin. In the filtrate from the main product a small amount of substance melting at 58.5° C. and solidifying at 51.5° C. was obtained; probably dipalmitin.

The main product was now analysed:

0.4742 gram gave 0.4349 gram palmitic acid = 91.71 per cent.

We had here presumably a mixture of one part tripalmitin and three parts dipalmitin, containing theoretically 91.42 per cent. of palmitic acid. We had met with a body of about this composition several times, and it was interesting to ascertain whether the mix-

[1] All of these bodies melting in the neighborhood of 59° C. and solidifying near 51° C. are doubtless slightly impure forms of dipalmitin, although it is quite possible that traces of polyglycerides should be formed by the long heating and the high temperature employed.

ture was a constant and more or less stable one or merely the result of chance. The substance was, therefore, again crystallised from hot alcohol, the middle portion of the yield only being saved. The product still melted at 68–69° C., and began to solidify in beautiful crystals at 67°, although the crystallisation was not complete until 65–64° C.

Analysed, the product yielded 91.50 and 91.80 per cent. of palmitic acid.

It is plain, then, that we have to do here with a well-defined mixture of three parts of dipalmitin and one part of tripalmitin, a mixture which would seem to be something more than a mere mechanical union of the two bodies, since repeated crystallisation changes neither the composition nor melting point of the body. In crystallising the substance from hot alcohol, however, it sometimes appeared as if a small portion was broken apart, as it were, the tripalmitin remaining undissolved, while the corresponding amount of dipalmitin was found afterwards in the filtrate.

In solubility this body stands about midway between di- and tripalmitin.

(*a*) In 100 parts of absolute alcohol there was dissolved in 2 hours at 21.5° C. 0.0860 part of the substance.

(*b*) Warmed with alcohol until completely dissolved, then allowed to stand for two hours and filtered at 21.5° C., there was dissolved in 100 parts of alcohol 0.1298 part of the substance.

Again, this same body was met with in an attempt to prepare dipalmitin. Here repeated efforts were made, by fractional crystallisation, to separate the two bodies. All five of the fractions, however, melted at about 68.5–70° C. and solidified at 67–68° C., while analysis of two of the fractions showed 91.68 per cent. and 91.33 per cent. of palmitic acid respectively, theory requiring 91 42 per cent. In still another case the same body was found with a melting point of 68° C., solidifying at 66° C., and with a content of 91.63 per cent. of palmitic acid.

Again, a large amount of this same mixture was obtained in an attempt to purify a quantity of the palmitins obtained by Berthelot's process, with the same melting point of 69–70° C., solidifying at 68° C., and with a content of 91.56 per cent. of palmitic acid.

Hundeshagen[1] mentions that in working with the stearins he found it comparatively easy to free distearin from any admixture

[1] Journal für prakt. Chem. **28**, 228.

either of stearic acid or of monostearin, but that tristearin could be separated only with extreme difficulty, or not at all. He mentions, moreover, a mixture, which he met with, possessing a melting point of 58° C. and showing on analysis a content of 93.04 per cent. of stearic acid, corresponding to about equal molecules of the two bodies, and that even after repeated crystallisations it showed the same melting point and composition. With the palmitins the only mixture we have met with at all constant is the one already mentioned.

Following Berthelot's plan we attempted the preparation of dipalmitin. Equal weights of water-free glycerin and palmitic acid (30 grams) were heated at a low temperature (about 100° C.) for 114 hours, then treated with lime and extracted with ether. 7 grams of a fat were obtained, melting at 62–63° C., and solidifying at 55.5° C., with a content of 89.76 per cent. of palmitic acid. The analysis by itself would lead one to suppose that we had here nearly pure dipalmitin, but further investigation showed that such was not the case. By fractional crystallisation from warm alcohol several portions were obtained, one melting at 64° C. and solidifying at 61° C., another melting at 46–50° C.[1] and solidifying at 45° C. with a content of 91.90 per cent. palmitic acid.

It is thus evident that here as well as in the other cases, in spite of the low temperature employed, all three of the palmitins had been formed, though less tripalmitin than at a higher temperature.

Preparation of the three Palmitins when the Acid and Glycerin are mixed in atomic proportions.

An attempt was now made to see if better results could not be obtained by heating the acid and glycerin in atomic proportions. Three portions of palmitic acid, 30 grams each, were taken, and to each were added the requisite theoretical amounts of pure glycerin for the tri-, di- and mono-palmitin respectively, viz. 3.59 grams, 5.38 grams and 10.77 grams. All three mixtures were heated in small flasks with the tubular end under mercury. They were heated at 180–200° C. for 4 hours; at the end of which time, or even sooner, there appeared to be no further evidence of chemical action, no more water being evolved. The fats were then heated with lime and extracted with ether.

[1] Appeared to melt at 46° C., but remained so opaque it was hard to determine.

In the case of the tripalmitin a residue of fat was obtained weighing 20 grams, melting at 61–62° C. and solidifying at 47.5–48° C. On analysis, 94.14 per cent. of palmitic acid was found. A single extraction with warm alcohol sufficed to remove the admixture of lower palmitins. The tripalmitin so obtained showed on analysis 95.42 per cent. of palmitic acid, theory being 95.28 per cent. This is without doubt the easiest and quickest way of preparing tripalmitin synthetically; the yield large and the product pure.

Evaporation of the ether used in the extraction of the dipalmitin left 13 grams of residue, melting at 62° C. and solidifying at 54° C., with a content of 92.48 per cent. of palmitic acid. By crystallisation of this product from warm alcohol, and rejecting that which crystallised at first, a pure dipalmitin was obtained, with a content of 90.54 per cent. of palmitic acid. Still the yield was not large.

In the case of the monopalmitin, 10 grams of fat were obtained by evaporation of the ether, melting at 67–68° C. and solidifying at 59° C. Analysis showed it to contain 91.61 per cent. of palmitic acid, evidently containing a large proportion of di- and tri-palmitin.

It would thus appear from the foregoing a difficult, if not almost impossible, matter to form synthetically either mono- or di-palmitin without a greater or less admixture of tripalmitin, separable, however, by repeated crystallisations. If, however, the palmitic acid and glycerin are heated together at a *low* temperature for a long time, there is without doubt much less tripalmitin formed and apparently less danger of the formation of the three-fourth dipalmitin mixture.

Properties of the pure Palmitins.

Monopalmitin is described by Berthelot as crystallising from ether in needles or microscopic prisms, or in radiating groups with a common centre. Our preparations of monopalmitin showed approximately the same appearance, crystallising from ether in the form of rhombic plates, single and in bunches, sometimes very closely packed; some of the plates with very perfect edges, others serrated. From alcohol (absolute) the palmitin was inclined to separate in small spherules, sometimes aggregated into masses, showing no distinct crystalline form.

The melting point of monopalmitin Berthelot places at 58° C.[1] Observing, however, all of the precautions which he deems so

[1] Chimie Organique **2**, 75.

necessary to bring the fat into the same molecular state, and which is more essential for the palmitins[1] than the stearins, we have still been unable to obtain a monopalmitin with so low a melting point. All the preparations that we have obtained, with a content of palmitic acid closely accordant with theory, have melted at 63° C., becoming solid at 62.25–62.75° C.

Dipalmitin, Berthelot describes as crystallising in small tables and needles. Our preparations have crystallised from ether in warty masses, in which no distinct crystalline form could be observed. From alcoholic solutions, the fat separated in long curved needles, joined into branching groups with frequently small spherical masses of the fat attached to them.

The dipalmitin of Berthelot melts at 59° C. and solidifies at 51° C. All of our preparations of dipalmitin that possessed the requisite percentage of palmitic acid melted at about 61° C., solidifying at 57° C. Twice, however, we have obtained a palmitin with the theoretical percentage of palmitic acid, but with a constant melting point of 49° C., solidifying in the one instance at about 47° C., the other at 48° C.

Tripalmitin dissolved in hot alcohol, crystallised on cooling from dilute solutions in groups of irregularly shaped crystals. Crystallised from ether, tripalmitin appeared in the shape of irregular, doubly curved bodies, singly and crossed, in groups of two or more; from more dilute solutions frequently appearing in the form of smaller and more closely aggregated bunches.

According to Berthelot, tripalmitin melts at 61° C., and solidifies at 46° C. One sample of tripalmitin that we obtained with a content of 95.14 per cent. of palmitic acid (theory 95.28), had a constant melting point of 62° C., solid at 45.5° C. Several other samples, however, with a percentage amount of palmitic acid closely agreeing with the theoretical, melted a degree or so higher, and solidified two degrees lower; for example, one melting at 63° and solidifying at 45°, still another melting at 64° C., and crystallising at 47° C.

In the case of this tripalmitin we had a very forcible illustration of the phenomena illustrating the isomeric modification of fats so admirably demonstrated by Duffy,[2] who found a natural tripalmitin in palm oil, with a solidifying point of 45.5° C. and with a melting point of three modifications, viz. 46° C., 61.7° C. and 62.8° C.

[1] Chimie Organique, 71, 72. [2] Jour. Chem. Soc. 5, 197; also Watt's Dictionary 2, 879.

In a somewhat similar manner our artificial tripalmitin, melting at 64° C., on being suddenly plunged into a heated bath, melted then at a temperature much below the original melting point. Thus by *plunging* the fat, which had been previously melted in a capillary tube and then suddenly cooled by exposure to the air, into a bath at different temperatures, it was found that the fat was not melted at 42° C., nor at 43° C., but when plunged suddenly into a bath at 45° C., it quickly became milky, and at 47° C., quite clear. As the temperature rose it again became solid, and remained so up to 64° C., when it again melted. On the other hand, when placed in a bath at 43° C., it did not melt when the temperature was *gradually* raised to 55° C., though when melted, quickly cooled, and then *plunged* into the same bath at 55° C. it melted at once.

After melting and sudden cooling in a capillary tube as described, the tripalmitin retained this low melting point for some time, even after standing for 24 hours at the ordinary temperature. This apparently constitutes a good illustration of the different physical modifications of the fat, as well as showing another point of similarity between the natural tripalmitin and the artificial body.

Maskelyne[1] likewise had a similar experience. He obtained a natural tripalmitin by the extraction of a vegetable fat with a mixture of alcohol and ether, which after repeated crystallisations showed a solidifying point of 49° C. This preparation he records melted at 50.5° C., then again became solid, and finally melted and remained so at 66.5° C.

The *three-fourths dipalmitin mixture* when crystallised from an etherial solution, appeared under the microscope in the form of small spherical masses, showing spicules over their surface. Crystallised from alcohol the bunches had the appearance of being composed of needle-shaped crystals, showing, therefore, more of the appearance of dipalmitin than tripalmitin. Hundeshagen[2] in his mixture of equal parts of di- and tri-stearin, states that the crystalline form of the substance varied from time to time, sometimes having more the appearance of the former, sometimes of the latter.

These many variations in the melting points of the individual fats noticed in our work, while undoubtedly due in part to slight impurities or admixtures, too small for analysis to detect, plainly indicate the existence of various physical modifications.

[1] Jahresbericht der Chemie **8**, 520.

[2] Journal für prakt. Chemie **28**, 229.

APPARATUS FOR THE DETERMINATION OF NITROGEN BY THE COPPER OXIDE METHOD, AND COMPARISON OF THIS AND THE RUFFLE METHOD.

By Charles W. Dabney, Jr., and B. von Herff.

The N. C. Agric. Experiment Station, Raleigh, N. C.

The determination of total nitrogen has become the most important operation which the agricultural chemist has to perform. Such high values are attached to the nitrogenous materials in superphosphates that small variations in the determination of nitrogen will make considerable differences in the valuations. It becomes necessary, thus, for the agricultural analyst to attain the greatest possible accuracy in his rapid routine work. Since the introduction of a great variety of different compounds of nitrogen into fertilizers, this problem has become quite a difficult one, and has caused us to try every new method and every improvement which has been suggested.

The two methods which we shall discuss here have each their merits, and both come reasonably near meeting all these requirements. These are the Ruffle method and the copper oxide, or so-called "absolute," method.

1. *The Ruffle Method.*—We have worked this very nearly as described by its author,[1] using Bohemian glass combustion tubing always, however. We have not tried the method without soda, or without hyposulphite, as has been suggested.

This method has the advantage of being simpler, cheaper and somewhat quicker than the copper oxide method. There are fewer risks to run, fewer combustion tubes break, and for several reasons a much larger per cent. of complete analyses are obtained by it.

The tube we have used was exactly like the ordinary soda-lime combustion tube. Charcoal, free from nitrogen, was obtained, and the mixture with sulphur was weighed out in 2 gram portions. The soda-lime and fused hyposulphite were mixed by eye. In making the combustion a noteworthy precaution is to heat the tube very slowly at first, especially in case of compounds containing high

[1] Journ. Chem. Soc. **39**, 87.

per cents of nitrogen. In some cases the determination may require three hours. If the combustion is too much hastened the results will be too low. Ordinarily we have found that an hour and a half is necessary for making two such determinations together, the weighing and filling the tubes included. Occasionally we have found the final reaction in titrating rather indistinct when this combustion had been made.

2. *The Copper Oxide Method.*—We have followed the method as described by Prof. Johnson[1] in the main. We have not found it necessary to pass oxygen, however, in most cases, and have, therefore, omitted the chlorate of potash from the end of the tube. In mixtures containing a good deal of horn, where resistant cyanogen compounds are formed, this oxygen may be of some aid in completing the combustion.

In analysing compounds rich in nitrogen, and especially those containing much nitrate, the addition of charcoal powder to the substance causes the nitrogen to come off more regularly, and gives generally better results.

For making two analyses together by this method we have found that about two hours are required. This depends, however, chiefly upon how the pump works. In making this estimate of the time required we refer to the pump described below, which never took more than ten minutes to complete the exhaustion.

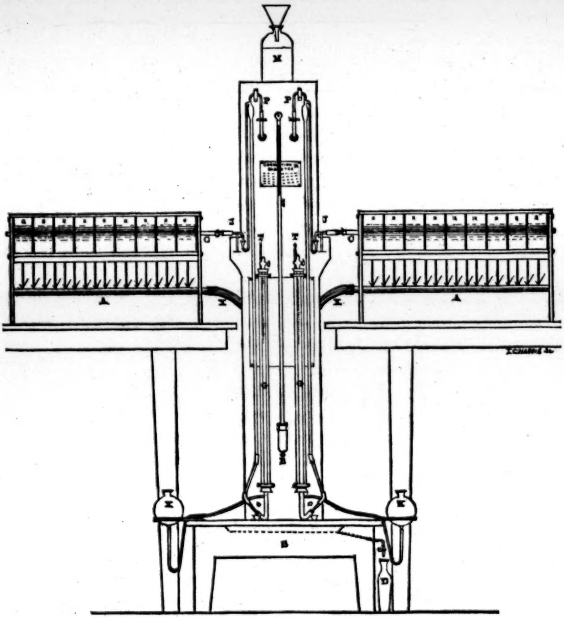
For getting the air, before combustion, and the nitrogen afterwards, out of the tube, we have used carbon dioxide without a pump and have obtained excellent results, though more time is consumed in this way than with a good pump. Magnesite or carbonate of manganese, put in the back end of the tube, are the best sources of carbon dioxide for this purpose. They give off their carbon dioxide slowly and uniformly. Bicarbonate of soda can be used also, though it is liable to give off its gas too suddenly.

In our experience this method of driving the nitrogen out is far preferable to working with a poor, or slow, pump. We recommend it to those who do not want to invest in a Sprengel pump. If you can get a fast-working, tight pump, a combination of both plans of getting the nitrogen out is the best and quickest method.

It was with some difficulty and after numerous trials of pumps of different forms that we got one which met all of the requirements.

[1] This Journal **2**, 27.

This pump, and the connected apparatus for making two nitrogen determinations at the same time, is shown in the figure.



The only glass part which it is necessary to have made by an expert glass-worker is the piece from P to rubber joint above O and its branch to J, with the ground-glass joint there. The little jet tube in the bulb is wanting in the cut. The length of tube from the bulb to O should be 1.2 m. The length of the branch to J will be regulated to suit the height of your table. The ground joint at J is a great convenience. If a perfect one cannot be obtained, it can be dispensed with and you can get the necessary play in the rubber joint, also indicated at J, which otherwise is omitted. A rubber band over a nail holds the connecting tube firmly into the ground joint.

The speed of the pump will depend much upon the calibre of the jet tube and its relation to that of the fall tube. In our best pump the relation is, internal diameter of the jet tube at smallest place 1.5 mm., internal diameter of fall tube 2.5 mm. The branch tube to J should have an internal diameter of about 2 mm.

The stand to which all of the apparatus is fastened has for its base a shallow box 70 x 70 x 10 cm. on legs, making it 35 cm. high. This is the mercury receiver, and it has an outlet with a pinch-cock at a place convenient for drawing the mercury in the flask D, for returning it to the reservoir M. The front half of the top of this box raises up as a lid. Two holes in the back half of it carry the funnels which catch the mercury. The upright frame is 1.3 m. high above top of base and is well braced behind. It is 25 cm. wide and has two holes at a convenient place for the stout rubber tubes which convey the mercury from the reservoir M to the pumps P P. The flow of mercury is controlled by a pinch-cock just below P. The mercury reservoir, M, is an extra strong 1 gal. aspirator bottle. The tubulature is behind for convenience.

The azotometer with its thermometer T and graduate G, connected with the potash solution reservoir K, which can be raised or lowered as desired, is that of Schiff, figured and described by Prof. Johnson in this Journal.[1] The water connections with the jacket of the azotometer are not figured, because they would complicate the cut, and because it is not necessary to pass water around the nitrogen graduate if one can wait an hour for all the parts to take a uniform temperature before taking the readings.

The barometer is hung conveniently between the pumps. The other details, the connection with the combustion tube C, in the furnace A, and the gas X need no explanation.

The glass parts, described above, were made by our specifications by Mr. Emil Greiner, manufacturer of scientific glass apparatus, 345 E. 18th street, New York city.

A pump of this kind meets all of the requirements of the case. It exhausts the combustion tube rapidly and is easy to manage. It is best to turn on the full head of mercury for the first two minutes and then gradually diminish the pressure by partially cutting off the stream. By evolving some carbon dioxide in the combustion tube after five minutes pumping, the last trace of air can be swept out of the tube in eight to ten minutes. The follow-

[1] *Loc. cit.*

ing results will illustrate the working of two pumps we have at the N. C. Experiment Station. Two ordinary combustion tubes of equal length were filled as for analysis and connected at ordinary temperature with the pumps, and the amounts of air removed from each in successive minutes were measured under equal temperature and pressure.

Minutes.	Pump No. 1. Cc. of Air Removed.	Pump No. 2. Cc. of Air Removed.
1	65.0	62.0
2	16.0	12.0
3	5.2	3.8
4	0.2	2.9
	86.4	
5		1.8
6		1.7
7		0.6
8		0.2
		85.0

As the careful worker will generally want to make two distinct determinations in each material, this arrangement of two complete and symmetrical sets of apparatus will be found to greatly promote comfort and save time.

Comparative results by the Ruffle and the Copper Oxide Methods.

Using the apparatus and methods described above, we have made a great many comparisons of these two plans of determining nitrogen. The following list of materials is selected to represent a wide range of substances:

1. Paranitrobenzanilid C_6H_4, NO_2, NH, $COC_6H_5 = C_{13}H_{10}N_2O_3$. Well crystallised, pure.

2. Nitrate of potash, KNO_3, pure, crystallised.

3. Nitrosalicylic acid C_6H_3, OH, NO_2, COOH $= C_7H_5NO_5$. Pure, well crystallised.

4. Dinitrophtalyltoluidid, C_6H_2, CH_3, $(NO_2)_2$, $N(CO)_2C_6H_4 = C_{15}H_9N_3O_6$.

5. An ammoniated cotton fertilizer, animal ammoniate and a small amount of nitrate of soda.

6. A fertilizer containing tobacco stems and dust (in which we

have found nitrates), fish-scrap, and small amounts of sulphate of ammonia and Peruvian guano.

7. An ammoniated superphosphate, said to contain 1 per cent. of nitrogen from nitrate.

8. A superphosphate ammoniated with animal matter, vegetable matter, and it was said 0.5 per cent. nitrogen from nitrate.

9. Shoemaker's bone meal, from bone extracted with naphtha.

10. Ordinary North Carolina fish-scrap.

11. Cotton-seed meal extracted with naphtha, quite dry and free from oil; from Shoemaker, Philadelphia.

12. Peruvian guano, said to be Chincha Island.

13. Shoemaker's "Ammonite B," mostly extracted muscular tissues of various animals.

14. Dried red blood, from Shoemaker.

Two Ruffle determinations, made at the same time, are given for each substance. The two nitrogen per cents were made by the copper oxide method in duplicate, as described above. All of the determinations in each column were conducted as nearly as possible in the same way. No charcoal was used or oxygen passed in the copper oxide determinations. The results are not all as near together or as near the calculated per cents as they should be, but they serve to show what the methods will do when followed blindly and unvaryingly. When special precautions were used, as the mixture of charcoal directly with nitro compounds, better results were obtained.

In the column of differences between averages of Ruffle results and averages of copper oxide results, Ruffle is + and copper oxide is —. Copper oxide gives results mostly a little higher than Ruffle.

These analyses and many others in our possession show that in fertilizers containing small amounts of nitrogen, the Ruffle method and the copper oxide method give equally good results. By the copper oxide method the errors are apt to be in the direction of too much, by the Ruffle method in the direction of too little.

In substances containing larger amounts of nitrogen the differences are greater. Such substances undoubtedly require special precautions. Highly nitrated compounds should have charcoal or sugar mixed with them, &c.

In general it may be said that the Ruffle method is as well suited

Comparison of Ruffle and Copper Oxide Methods of Determining Nitrogen.—Dabney and von Herff.

Number.	Material.	Ruffle Method.			Copper Oxide Method.			Difference between Ruffle and Copper Oxide.	Nitrogen Calculated.	Error by Ruffle Method.	Error by Copper Oxide Method.
		Nitrogen per cent.	Difference.	Average.	Nitrogen per cent.	Difference.	Average.				
1	Paranitrobenzanilid	11.45 11.54	0.09	11.495	11.70 11.64	0.06	11.670	— 0.175	11.570	— 0.075	+ 0.100
2	Nitrate of potash	13.75 13.72	0.03	13.735	13.65 13.75	0.10	13.70	+ 0.035	13.861	— 0.126	— 0.161
3	Nitrosalicylic acid	7.50 7.40	0.10	7.450	7.69 7.62	0.07	7.655	— 0.205	7.690	— 0.24	— 0.04
4	Dinitrophtalyltoluidid	12.59 12.65	0.06	12.620	12.85 12.97	0.12	12.910	— 0.29	12.844	— 0.224	+ 0.066
5	Ammoniated cotton fertilizer	2.10 2.07	0.03	2.085	2.06 2.07	0.01	2.065	+ 0.020			
6	Fertilizer, with tobacco refuse	2.10 2.15	0.05	2.125	2.21 2.18	0.03	2.195	— 0.07			
7	Ammoniated superphosphate with 1 p. c. N from nitrate	2.10 2.12	0.02	2.110	2.11 2.04	0.07	2.075	+ 0.035			
8	Ammoniated superphosphate with animal and vegetable matter and nitrate	2.10 2.06	0.04	2.080	2.08 2.11	0.03	2.095	— 0.015			
9	Shoemaker's bone meal	6.74 6.69	0.05	6.715	6.73 6.82	0.09	6.775	— 0.060			
10	N. C. fish-scrap	7.52 7.49	0.03	7.515	7.64 7.71	0.06	7.675	— 0.160			
11	Cotton-seed meal, extracted	7.79 7.94	0.15	7.865	8.06 8.09	0.03	8.075	— 0.210			
12	Chincha Island Peruvian	7.21 7.30	0.09	7.255	7.27 7.27	0.00	7.270	— 0.015			
13	Shoemaker's "Ammonite B"	12.65 12.72	0.07	12.685	12.73 12.71	0.02	12.725	— 0.035			
14	Dried blood	14.60 14.57	0.03	14.585	14.85 14.69	0.16	14.770	— 0.185			

to the general uses of the chemical laboratory as the copper oxide, or so-called "absolute" method. The latter method, with the aid of the apparatus described above, leaves, however, little to be desired, so that it may be said now that we have two almost equally available and convenient "absolute" methods which can be used to check each other.

CONTINUOUS ETHERIFICATION.

By L. M. Norton and C. O. Prescott.

Since the examination of the process of continuous etherification by Williamson,[1] and the explanation of it in his classical research, our knowledge of its possible applications has made no material progress. The formation of ethers by the action of sulphuric acid upon alcohols has found practical application only in the manufacture of ethyl ether in the manner proposed by Boullay[2] before the course of the reaction was understood, and in the manufacture of methyl ether,[3] which is now used extensively for cooling purposes. We have re-examined the formation of ethyl ether by this process in order to fix more carefully the limits of temperature within which the reaction can be effected, and also the temperature at which etherification is most complete, and we have also investigated the behavior of propyl, isobutyl and isoamyl alcohols when subjected to the process of etherification. We have examined also the formation of mixed ethers by this process.

Ethyl Alcohol.

The apparatus used in all the experiments described below was essentially that originated by Boullay, and afterward used by Williamson. It consists of a two-litre flask, with a wide mouth closed by a cork through which passes a thermometer, a drop-

[1] Ann. d. Chem. **77**, 37, and **81**, 73. [2] Jour. Phar. **1**, 96. [3] Tellier, Arch. Phar. **16**, 57.

funnel, and a delivery tube leading to a condenser cooled continually with ice water.

In the first series of experiments 200 grams of commercial 90 per cent. alcohol were subjected to etherification in each experiment. Twenty grams of alcohol were mixed with 36 grams of ordinary strong sulphuric acid, placed in the flask, which was then heated to the desired temperature in an oil-bath, and the mixture was maintained at the desired temperature while the remaining alcohol was slowly added through the drop-funnel. It is evident that if the distillate was subjected to fractional condensation and the undecomposed alcohol returned to the generating flask and only the ether collected, in sufficient time the alcohol would be changed to ether, even at a temperature far too low for advantageous etherification. As we desired to examine the amount of alcohol changed to ether at different temperatures we allowed the ether and undecomposed alcohol to distill together from the generating flask, and subsequently subjected the distillate to fractionation. The distillates from temperatures below 160° were free from sulphurous anhydride. They were treated with solid caustic potash to remove any traces of sulphuric acid and then distilled from quick-lime. After three fractionations, the portions boiling between 35° and 45° were weighed. In these experiments 163 grams of pure ethyl alcohol were available for etherification.

Temperature of formation.	Weight of ether obtained.	Per cent. of theoretical yield of ether,
120°–125°	12 grams.	7.35 per cent.
125°–130°	27 "	16.55 "
130°–135°	45 "	27.58 "
135°–140°	45 "	27.58 "
140°–145°	47 "	28.81 "
145°–150°	47 "	28.81 "

A second series of experiments was now made, and the distillates were fractionated with the utmost care. In these experiments 150 grams of 90 per cent. alcohol were used, and 118 grams of ethyl alcohol were available for etherification. The specific gravity of the ether obtained was 0.744 at 0° compared with water at the same temperature. This specific gravity would indicate the presence of a minute quantity of alcohol in the ether.

Temperature of formation.	Weight of ether obtained.	Per cent. of theoretical yield of ether.
115°–120°	5 grams.	4.2 per cent.
120°–125°	10 "	8.4 "
125°–130°	20 "	16.8 "
130°–135°	33 "	27.7 "
135°–140°	43 "	36.1 "
140°–145°	52 "	43.6 "
145°–150°	47 "	39.5 "
150°–155°	49 "	41.0 "
155°–160°	48 "	40.3 "
160°–165°	? "	

These results would indicate that the action of alcohol upon ethylsulphuric acid begins at a temperature much lower than has been supposed, rises in rapidity and completeness until the temperature of 145° is reached, where the maximum yield of ether is obtained. Above 150° the yield begins to lessen, and doubtless the formation of ethylene begins, but the yield does not diminish greatly until 160° is reached. At 160° the formation of sulphurous anhydride begins and numerous gaseous products are evolved, and the sulphuric acid is soon destroyed, as has been observed by others.[1] Ether continues to be formed above 160° in small quantities, and, according to Mitscherlich,[2] is even found among products formed at 200° and above that temperature.

Propyl Alcohol.

We were unable to find any evidence that this alcohol was ever subjected to the process of continuous etherification. We took 50 grams of propyl alcohol for our experiment. Fifteen grams were mixed with 20 grams of sulphuric acid, the mixture heated at 135°, and the remaining alcohol added in the usual way. A colorless distillate was obtained, at the same time there was a slight evolution of sulphurous anhydride and a slight deposition of tar in the generating flask. The distillate was treated with solid caustic potash, then distilled from lime, and was found to boil between 80° and 90°. It was next washed with water, distilled again from lime, and then allowed to stand with sodium until all action ceased. Its boiling point was then between 82° and 84°; it possessed a strong

[1] Gmelin, Handbuch **4**, 552. [2] Ann. Ch. Phys. **3**, 7, 12.

etherial odor, and agreed in all respects with the propyl ether described by Chancel [1] and Linneman.[2] The yield is very good, and this method will prove the most convenient for the preparation of propyl ether.

Isobutyl Alcohol.

It is well known[3] that at a high temperature sulphuric acid withdraws water from isobutyl alcohol and produces isobutylene. We have subjected isobutyl alcohol to the ordinary process of continuous etherification at 120° and also at 135°. In both cases sulphurous anhydride was freely evolved, and tar remained in the generator.

A yellowish distillate was obtained, which upon purification and fractionation proved to consist of undecomposed isobutyl alcohol. We were unable to obtain any appreciable quantity of isobutyl ether.

Isoamyl Alcohol.

We next investigated the behavior of isoamyl alcohol under the ordinary conditions of continuous etherification. At temperatures very little above 100° a violent action begins, and sulphurous anhydride is freely evolved. Before the temperature of 140° can be reached the sulphuric acid is destroyed, and only tar remains in the generator. As isoamyl ether boils at 176° it is evident that it cannot be produced by this method. Below 140° a distillate was obtained, which proved to contain undecomposed isoamyl alcohol and hydrocarbons of the CnH_{2n} series. We were unable to confirm the statement of Balard[4] that small quantities of isoamyl ether are formed by the action of sulphuric acid upon isoamyl alcohol.

Methyl and Ethyl Alcohols.

The authority for the statement that mixed ethers can be obtained by the process of continuous etherification rests upon two experiments of Williamson.[5] It seemed desirable to test the applicability of this process to the formation of mixed ethers anew, especially as Guthrie[6] was unable to repeat one of Williamson's experiments. We chose for an experiment a mixture of methyl and ethyl

[1] Ann. d. Chem. **151**, 304.
[2] Linneman, Ann. d. Chem. **161**, 37.
[3] Lermontoff, Ann. d. Chem. **196**, 117, *et al.*
[4] Ann. d. Chem. et Phys. **3**, 12, 294.
[5] Ann. d. Chem. **81**, 77.
[6] Ann. d. Chem. **105**, 37.

alcohols, containing 1 mol. of CH_3OH to 1 mol. of C_2H_5OH. This mixture was treated in the usual manner at 140°, and the utmost care observed in condensing the products. A colorless distillate, free from sulphurous anhydride, was obtained, and at the same time a gas, which we were unable to condense, escaped from the apparatus. This gas possessed a strong etherial odor, and was doubtless methyl ether, which boils at —23°. The distillate resolved itself upon fractionation into three portions, one boiling from 10°–15°, the second from 30°–40°, and a third portion consisting of undecomposed alcohols. We obtained from the portion boiling lowest a considerable quantity of a liquid boiling between 10° and 13°, possessing a strong etherial odor, and corresponding in every respect with the methyl-ethyl ether prepared by Williamson[1] from sodium alcoholate and methyl iodide, and also by Würtz,[2] by the action of a mixture of methyl iodide and ethyl iodide upon silver oxide. The portion of the distillate boiling between 30° and 40° consisted mainly of ethyl ether. The yield of the mixed ether was very good. The three possible ethers appear to be formed simultaneously, but the mixed ether is formed in much the largest proportion.

Ethyl and Propyl Alcohols.

A mixture of equivalent parts of these alcohols was next treated in the usual manner. A colorless liquid was obtained, which resolved itself upon fractionation into ethyl ether, a mixture of ethyl and propyl alcohols, and a portion boiling between 60°–80°. The portion boiling between 60° and 80° was washed with water, distilled from quick-lime, and finally treated with an excess of sodium to remove any alcohols present, and rectified. The liquid then boiled between 66° and 68°, and possessed an etherial odor, and gave the following results upon analysis: 0.2286 gram of substance furnished 0.5620 gram of CO_2 and 0.2827 gram of H_2O.

	Theory for $C_3H_7OC_2H_5$.	Found.
C	68.17	67.04
H	13.64	13.74

The analysis leaves no doubt that the substance is the ethyl-propyl ether which was first prepared by Chancel[3] by the action of ethyl iodide upon propyl alcohol and caustic potash.

[1] Ann. d. Chem. **81**, 77. [2] Ann. Ch. Phys. **3**, 46, 222. [3] Zeit. f. Chem. 1869, 367.

Ethyl and Isobutyl Alcohols.

Equivalent parts of these alcohols were subjected to the usual treatment. Sulphurous anhydride was freely evolved, and a yellow distillate with a very disagreeable odor obtained. The distillate consisted almost entirely of undecomposed alcohols and no ether could be obtained from it. The mixture behaved exactly as did the isobutyl alcohol alone.

Methyl and Isoamyl Alcohols.

Methylisoamyl ether was prepared by Williamson[1] by the continuous etherification of a mixture of these alcohols. We repeated his experiments, following his directions with the utmost exactness. Sulphurous anhydride was evolved in large quantities. In the distillate obtained we found undecomposed alcohols and products similar to those obtained from isoamyl alcohol alone under like conditions, but were unable to detect the presence of methylisoamyl ether. We made repeated attempts at 135° and 140°, but the distillate in every case consisted almost entirely of the alcohols which had distilled undecomposed as soon as the sulphuric acid had been all reduced. An attempt by Guthrie[2] to obtain ethylisoamyl ether by continuous etherification, in the manner described by Williamson, gave similar results, and Guthrie was unable to obtain the ether by this method. As our experiments show that etherification does not take place to any extent, certainly in the case of ethyl alcohol, below 105°, and as isoamyl alcohol decomposed sulphuric acid with the evolution of sulphurous anhydride at that temperature, it is evident that the ordinary process of continuous etherification can only be applied to the formation of the simple and mixed ethers from the simplest alcohols, and it is not probable that it can be used satisfactorily for the etherification of alcohols containing more than three atoms of carbon.

Mass. Institute of Technology, Boston.

[1] Ann. d. Chem. **81**, 77.

[2] Ann. d. Chem. 105, 37.

Communications from the Chemical Laboratory of Rutgers College.

XIII.—NOTE ON OZOCERITE.

By Franklin S. Smith.

In the clay fields of Mr. Otto Ernst, of South Amboy, N. J., specimens of Ozocerite have recently been found. In a letter, Mr. Ernst writes: "I do not think it likely that I shall find any paying quantities of it, though I recollect finding a lump ten times as large some years ago. Its low specific gravity probably carried it here by waters from the petroleum fields."

The specimen was in the form of an irregular lump, about three-quarters of an inch in its longest diameter. The color was nearly pure.

A combustion gave:

		Calc. for C_8H_{10}.
Carbon	86.46	85.71
Hydrogen	12.83	14.29
	99.29	

The substance was not purified, so that the above results are, of course, only approximate. There is little doubt, however, that the hydrocarbons belongs to the series C_nH_{2n} as stated by Grabowski.

XIV.—NOTE ON SILICIOUS EARTH.

By J. W. McKelvey.

In a small basin on the farm of Mr. D. Judson Cook, which is located near Drakesville, Morris County, New Jersey, there is a deposit of infusorial earth which covers about three acres. The first stratum, which begins at the surface, is peaty to a depth of about one foot. The next is infusorial earth to a depth of three feet, and then come seven feet of a white, sandy clay. At the bottom of this there is a deposit of gravel and cobble-stone drift. The white clay seems to be a mixture of clay and infusorial earth. Near the edge of the bed it grows thin, and the upper fifteen inches of the three feet layer are more porous than the rest.

This infusorial earth is of a grayish-white color, and on igniting becomes perfectly white. It contains small fragments of leaves and twigs.

The specific gravity of the sample was 1.11. On analysis it gave:

Silica	80.66 per cent.
Alumina	3.84
Lime	.58
Loss on ignition	14.01
	99.09

NEW BRUNSWICK, N. J.

ANTHRACENE FROM WATER-GAS TAR.

BY ARTHUR H. ELLIOTT.

The presence of aromatic hydrocarbons in the products resulting from the destructive distillation of petroleum and its allies has been proved by quite a number of experimenters. L. Prunier[1] treated the products of the distillation of petroleum with bromine, and found that those coming off at low temperatures did not absorb this element, while the products coming off at higher temperatures readily absorbed it, and contained the aromatic hydrocarbons, anthracene, pyrene, chrysene, fluoranthrene, acetnaphthene, petrocene and carbpetrocene, together with ethylenes and acetylenes.

Liebermann and Burg[2] found that by passing the heavy oils resulting from petroleum and paraffine refining through red-hot tubes they obtained a mixture of hydrocarbons similar to ordinary coal tar, and containing four per cent. of benzol and toluol with nine-tenths of one per cent. of crude anthracene. Petroleum yielded benzol but no anthracene. Salzmann and Wichelhaus[3] obtained similar results.

All these experimenters worked upon the products of destructive distillation carried on in small apparatus in the laboratory. But the

[1] Ann. Chim. Phys. (5), **17**, 5. Jour. Chem. Soc. **36**, 1025.
[2] Berichte deutsch. chem. Ges. 1878, 723.
[3] Berichte deutsch. chem. Ges. 1878, 802 and 1431.

tar produced by passing heavy petroleum over wood heated to redness on a large scale, was examined by Letny.[1] After several passages through the red-hot tubes it was found that the tar contained benzol, toluol, xyol, naphthalene, anthracene, phenanthrene, and unchanged petroleum. By passing heavy petroleum through a small tube heated to redness and filled with charcoal Letny obtained amylene, benzol, toluol, xylol, and oils boiling at higher temperatures, but no solid hydrocarbons.

Rudnew[2] says, that at the Kasan Gas Works the tar resulting from the manufacture of petroleum gas is distilled in the ordinary way. It yields ten to twenty per cent. of benzol, and five per cent. of naphthalene, together with anthracene; but he does not give the percentage of the latter.

A little more than a year ago I obtained some of the tar formed during the manufacture of so-called water-gas. It was already known to me that this tar contained naphthalene in very large quantities, and it appeared most probable that other hydrocarbons of the aromatic series were also present, more especially anthracene. Since anthracene is the most valuable of the higher members of the aromatic hydrocarbons, from its use in the production of alizarine—and the day is not far distant when water-gas will be used more extensively, at least in the United States—the value of water-gas tar for the manufacture of anthracene appeared to me of considerable importance. My first efforts were confined to the distillation of the tar, and an examination of that part of the distillate that comes over at 210° to 350° Celsius. This distillate was dissolved in glacial acetic acid, and gave a clear solution; which was treated with a mixture of chromic acid dissolved in a mixture of acetic acid and water, according to the well-known method of Lück. After digesting some hours, the mixture was poured into water and a flocculent precipitate separated. This precipitate having all the appearance of anthraquinone, was thoroughly washed with water, then with dilute solution of sodic hydrate, and finally with water again. The result of this experiment was that that part of the tar distillate coming over between 210°–350° contained 5.8 per cent. of anthracene.

The distillation which gave the above results was continued still further until the contents of the retort became coked. The distillate thus obtained was treated with glacial acetic acid the same as

[1] Ding. Jour. **229**, 353. [2] *Ibid*, **239**, 72.

the above; but only 32.7 per cent. of it was dissolved. The resulting solution was treated with chromic acid dissolved in acetic acid as described before, and the anthraquinone obtained was equal to 2.08 per cent of anthracene in the distillate obtained from 350° Celsius to coking.

In the next experiment I took a measured quantity of tar, 340 cubic centimetres, and obtained a small quantity of oil distilling over below 200° Celsius. The distillation was continued until the contents of the retort were thick pitch. This gave a distillate which was a mixture of oil and solid crystalline matter, amounting to 52.9 per cent. of the original tar. The oil was carefully poured off from the solid part of the distillate, and the latter was treated with petroleum spirit (boiling point 65°–105° C.). The solids thus washed were of a pale yellow color and equal to 3.97 per cent. of the original tar. These solids were dissolved in glacial acetic acid, and treated with chromic acid in the manner before stated. The resulting anthraquinone was equal to 2.90 per cent. of anthracene in the original tar.

From these experiments it became evident that this tar was particularly rich in anthracene, and I determined to pursue the experiments still further, but time did not permit until this summer, when I have again made an examination of quite a number of tars from the manufacture of water-gas.

These tars have a specific gravity ranging from 1.080 to 1.100, are liquid at summer temperatures, and more or less solid during the winter.

Taking one of the dense tars the following results were obtained: The specific gravity was 1.100. For distillation 400 cubic centimetres were taken, and gave the following fractions and weights per hundred volumes of tar distilled:

Temperature, Degrees Celsius.			Weight of Distillate from 100 volumes.
80 to 200	...	...	9.2 { ⅓ Oil. ⅔ Water.
200 " 270	...	...	{ 11.2 Solid. 17.7 Oil.
270 " Pitch	...	...	{ 6.0 Solid. 26.5 Oil.
Last fraction	...	...	{ 1.7 Semi-solid. 6.0 Oil.
		Total	78.3

The fraction coming over between 80 and 200 degrees consisted of a mixture of oil and water, and was reserved for future examination. The second fraction between 200 and 270 degrees Celsius was filtered and the oil pressed from the solid part between sheets of filter paper. The pressed solids were crystalline, and were dissolved in glacial acetic acid and treated with chromic acid according to the method of Lück. This gave only .82 per cent. of anthracene, which is equivalent to .09 per cent. on the original tar. The oil from these pressed solids had a specific gravity of 1.030; it was not examined for anthracene because the pressed solids had given so little of this hydrocarbon. The pressed solids are practically all naphthalene, and the oil yields no phenol when treated with alkalies.

The third fraction coming over at 270 degrees to near the end of the distillation was filtered and the oil pressed out with filter paper as in the case of the second fraction. The pressed solids were of a greenish-yellow color and of low melting point. They were treated with about four times their weight of petroleum naphtha (boiling point between 65 and 105 degrees Celsius) to obtain crude anthracene. This crude anthracene had a melting point of 155° Celsius, and was equal to 18.6 per cent. of the pressed solids. By treatment with chromic and acetic acids it was found to contain 85.1 per cent. of its weight of pure anthracene, which is equal to 15.83 per cent. on the pressed solids. But an examination of the wash petroleum naphtha showed that much anthracene had gone into solution, therefore a direct determination of anthracene in the pressed solids was made, without previous treatment with petroleum naphtha. It was now found that the pressed solids really contained 25.6 per cent. of pure anthracene, which is equivalent to 1.54 per cent. on the original tar.

The oil from the pressed solids of the distillate coming over above 270° had a specific gravity of 1.080, and by treatment with acetic and chromic acids gave 3.0 per cent. of pure anthracene, which is equivalent to 0.79 per cent. on the original tar.

The last fraction was obtained only a few minutes before stopping the distillation and when the contents of the retort were in a viscous condition. This fraction was filtered, and the crystalline mass of oil and solids left on the filter was treated with petroleum naphtha; the amount being too small to submit it to pressure with filter paper. By this treatment the semi-solids

gave 2.0 per cent. of their weight of crude anthracene, which is equivalent to 0.15 per cent. on the original tar. This crude anthracene had a bright orange color, but was too small to submit to the chromic acid treatment. The oil from the last fraction was treated with chromic and acetic acids, and gave 1.81 per cent. of its weight of pure anthracene, which is equivalent to .11 per cent. on the original tar.

The anthraquinone resulting from the treatment with chromic acid had all the properties necessary to its identification. It was of a pure white color, melted at 272° Celsius, and gave beautifully fine crystalline needles by sublimation, and also by solution in benzol. Analysis gave 80.08 per cent. of carbon and 5.14 per cent. of hydrogen; theory requiring 80.77 per cent. of carbon and 4.76 per cent. of hydrogen. This analysis is not as good as it should be, and the small quantity of material at my disposal is the only reason for presenting it. Nevertheless it is sufficiently close to help to identify the anthraquinone in connection with the other properties mentioned and the circumstances of formation.

The total anthracene obtained was equal to 2.63 per cent. on the original tar.

Former experimenters on this class of tars have been satisfied to simply detect the presence of anthracene, or, as in the case of Liebermann and Burg, to record the crude anthracene found. These last gentlemen found 0.9 per cent. in tar obtained from heavy oils from petroleum refining, and assuming that this crude anthracene contained 50 per cent. of pure hydrocarbon, the result is only 0.45 per cent. on the tar they used. Ordinary coal tar obtained in the destructive distillation of bituminous coal for gas contains only 0.3 to 0.4 per cent. of anthracene, while the tar I have described contains four or five times that amount.

Perhaps the most interesting fact in connection with this water-gas tar is that it is the result of the destructive distillation of light petroleum naphtha. This naphtha consists of those members of the marsh-gas series of hydrocarbons boiling below 150°, and consequently entirely free from the more or less solid paraffines found in the heavy oils used by other experimenters.

As time permits I hope to examine these tars still further, and at some future date will give an account of other constituents.

School of Mines, Columbia College, N. Y., *September*, 1884.

ON THE ACTION OF SODIUM PHENYLSULPHINATE ON METHYLENE IODIDE.

By Arthur Michael and George M. Palmer.

In the continuation of a research[1] on the influence of acid radicals containing sulphur on the hydrogen of the adjacent methylene, we endeavored to prepare methylenephenylsulphone by the action of sodium phenylsulphinate on methylene iodide. These experiments led to very unexpected results, which we deem of sufficient interest to describe in a separate note.

To an alcoholic solution of 8 grams (2 mols.) of phenylsulphinic acid, 1.4 grams (1 mol.) of sodium dissolved in absolute alcohol was added, and 7.4 grams (1 mol.) of methylene iodide. The mixture was heated in a flask, connected with a reversed cooler, for four hours on a water-bath. An examination of the contents of the flask showed that no reaction took place under the above-described conditions.

We then made a number of experiments on heating the same mixture in sealed tubes at a higher temperature, and found that a reaction ensued, and was completed by heating four or five hours at 120°. The contents of the tubes were brought in an evaporating dish, the alcohol driven off, and water added to the residue. The oil which separated on addition of water soon solidified, and the substance, after being pressed between bibulous paper, crystallised from alcohol. The substance contained iodine and sulphur. The analyses gave the following results:

I. 0.5070 gram of substance gave 0.1152 gram of H_2O, and 0.5587 of CO_2.

II. 0.3120 gram of substance gave 0.2715 gram of $BaSO_4$ (Russel's method).

III. 0.2584 gram of substance gave 0.2260 gram of $BaSO_4$ (Russel's method).

IV. 0.5147 gram of substance gave 0.5083 gram of $BaSO_4$.

V. 0.2105 gram of substance gave 0.1740 gram of AgI. (After Carius.)

VI. 0.3375 gram of substance gave 0.2815 gram of AgI. (After Carius.)

[1] This Journal **5**, 116.

	Theory for $C_6H_5SO_2CH_2I$.	Found. I.	II.	III.	IV.	V.	VI.
C	29.8	30.0					
H	2.4	2.5					
S	11.3		11.9	11.7	11.7		
I	45.0					44.7	45.

These results prove that the compound obtained by heating sodium phenylsulphinate with methylene iodide under the above-mentioned conditions, is formed by the replacement of one of the iodine atoms of the latter compound by phenylsulphone, a reaction represented by the following equation:

$$CH_2I_2 + C_6H_5SO_2Na = C_6H_5SO_2CH_2I + KI.$$

Methylene-iodophenylsulphone crystallises from alcohol as rhombic prisms with truncated end faces, melting at 64.5°. It is insoluble in boiling water, somewhat soluble in cold alcohol, readily in hot ether, and benzene dissolves it readily in the cold. It is evident that but one-half of the sodium phenylsulphinate employed in the above experiments entered into the reaction, and the following experiment shows that the iodo-sulphone is also formed when the sodium salt and methylene iodide are used in the proportion of their molecular weights.

Four grams (1 mol.) of $C_6H_5SO_2H$, 0.7 gram of sodium dissolved in alcohol and 7.4 grams (1 mol.) of methylene iodide were heated in a sealed tube at 120° and the contents of the tube treated in the above-described manner. We obtained a very good yield of methylene-iodosulphone, melting at 64.5°.

We next endeavored to effect the complete replacement of the iodine of methylene-iodide by phenylsulphone by heating an alcoholic solution of sodiumsulphinate and iodide, in the proportion of two equivalents of the first to one of the latter, at higher temperatures, and here too we met with very unexpected results.

This solution was heated in a sealed tube to 140° without any reaction taking place. Heated to 180° for several hours, the contents of the tube were brought into an evaporating dish and heated until the alcohol was driven off. The residue was extracted with water, and the insoluble portion crystallised several times from alcohol. The substance does not contain iodine.

The analyses gave the following results:

0.2559 gram of substance gave 0.4979 gram of CO_2 and 0.1370 gram of H_2O.

0.2355 gram of substance gave 0.4590 gram of CO_2 and .1109 gram of H_2O.

	Theory for $C_6H_5SO_2CH_2$.	Found. I.	II.
C	53.8	53.5	53.3
H	5.1	5.9	5.2

The substance crystallises from hot water as large tabular plates, melting at 88°. It is very soluble in cold benzene, alcohol and acetic ether, insoluble in cold water and alkalies. This substance is formed from methylene-iodophenylsulphone by the replacement of iodine by hydrogen, and, as we have shown further on by its synthesis, is methylphenylsulphone. The same compound is obtained in the action of sodium phenylsulphinate on methylene-iodophenylsulphone. An alcoholic solution of these substances, in equivalent proportions, gave a good yield of methylphenylsulphone when heated in a sealed tube at 180°.

In order to give a decisive proof that the compound is methylphenylsulphone, we prepared that substance synthetically, by the action of methyliodide on sodium phenylsulphinate.

To an alcoholic solution of 8 grams (1 mol.) of phenylsulphinic acid and 8 grams (one mol.) of methyliodide, an alcoholic solution of 1.3 grams of sodium was added, and the mixture heated at 100°, until no further separation of potassium iodide was noticed. The product evaporated to dryness on a water-bath, treated with water and the residue crystallised from alcohol yielded methylphenylsulphone, melting at 88°, with all the properties of the compound obtained from methylene-iodophenylsulphone:

$$C_6H_5SO_2Na + CH_3I = C_6H_5SO_2CH_3 + KI.$$

It seemed possible that the replacement of the iodine of $C_6H_5SO_2CH_2I$ by organic radicals could be accomplished if the reactions took place at a lower temperature than is possible when using sodium phenylsulphinate, and, with this in view, we examined the action of ethyl, methyl and phenylsodium oxides on the iodo-sulphone.

With ethylsodiumoxide the reaction took place at 100°. An alcoholic solution of 0.45 gram (1 mol.) of sodium and 5 grams (1 mol.) of $C_6H_5SO_2CH_2I$ was heated in a flask, with reverse cooler, on a water-bath until the solution showed a neutral reaction. The contents of the flask were evaporated to dryness, water added to the residue and the insoluble substance crystallised from alcohol.

The substance obtained in this manner melted at 88°, and showed all the other properties of methylphenylsulphone.

The following analysis affords further proof:

0.2355 gram of substance gave 0.1109 gram of H_2O and 0.4979 gram of CO_2.

	Theory for $C_6H_5SO_2CH_3$.	Found.
C	53.8	53.2
H	5.1	5.1

A similar experiment using methylsodiumoxide was next tried. Four grams of $C_6H_5SO_2CH_2I$, 0.3 gram of sodium were dissolved in absolute methyl alcohol, and the mixture heated at 100° until it became neutral. The contents of the flask, worked up as already described, gave methylphenylsulphone.

With sodiumphenyloxide it was found necessary to heat in a sealed tube at a higher temperature, as no reaction took place in an open flask at 100°. Two grams (1 mol.) of $C_6H_5SO_2CH_2I$ and 0.9 gram (1 mol.) of C_6H_5ONa were dissolved in absolute alcohol, and the solution heated at 170°. This experiment gave methylphenylsulphone as the result of the reaction. We also made some experiments on the replacement of iodine of the iodo-sulphone by hydroxyl. Here we obtained an oil as the resulting product, which we shall make the subject of further investigation.

The reduction of an iodo-compound by the action of such substances as methyl or ethylsodium oxides is not without precedents, although, to our knowledge, the above-described reaction is the first certain instance of a mono-iodo-compound showing this property. We mention, as one of the few analogous reactions, the formation of methylene iodide by the action of ethylsodium oxide on iodoform.[1] The easy reducibility of iodine in both instances is obviously connected with the strong negative character of the iodo-compounds. It seems that the phenylsulphone group exercises a greater influence on the iodine atom than a second iodine, for we have obtained an oil which is undoubtedly methylene-oxyphenyl by the action of methylene iodide on phenylsodium oxide.

We wish, finally, to call attention to the fact of the formation of methylene-iodophenylsulphone, even though a large excess of sodium phenylsulphinate is used, as one of the most remarkable

[1] Butlerow, Annalen, **114**, 264. Schützenberger's chloro and iodo derivatives of acetic acid show similar properties, but the existence of these compounds seems doubtful.

instances of partial replacement of halogens, united with the same carbon atom, that is at present known in organic chemistry. It seems to us, irrespective of any hypothesis on the constitution of methylene iodide—and an explanation of the above fact is not likely to be given until an insight into intra-molecular dynamics is obtained—that a strict adhesion to facts permits of but one conclusion; and it is, that one of the iodine atoms of methylene iodide has a function different from the second; or, were it permissible to assume that the degree of replaceability be a measure of the force between the iodine and the carbon, then one of the iodine atoms of methylene iodide has a greater affinity for carbon than the other. H. Kolbe was the first to regard the difference in the behavior of the halogens of ethylene-halogen towards certain reagents, as proving a difference in the function of the halogens, but it is doubtful whether that eminent chemist would be willing to make the same assumption concerning the iodine of methylene iodide, since he regards the same hypothesis in regard to the chlorine of lead chloride as not justifiable, notwithstanding the formation of basic lead chloride by the action of ammonia on it.[1] There is, however, a notable difference between that reaction and the above-described, inasmuch as the basic lead chloride is insoluble, and for that reason, probably, less subject to the further action of the base, while in the latter reaction the iodo-compound remains in solution.

TUFTS COLLEGE, MASS., *Oct.* 11, 1884.

ON THE CONVERSION OF ORGANIC ISOCYANATES INTO MUSTARD OILS.

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

Although the close relationship existing between oxygen and sulphur is characteristically shown in a large number of organic compounds containing these elements, in not a few instances a striking dissimilarity is noticed between the oxygen and the cor-

[1] Kurzes Lehrbuch der Chemie, 136.

responding sulphur compound. Thus the tendency to polymerisation, which the cyanate and isocyanate show so markedly, is only shown by the sulphocyanates at a high temperature and is apparently altogether lost in the mustard oils. Another example is found in the formation of metallic sulphocyanates by the addition of sulphur to cyanides, whereas the corresponding experiment with oxygen would have led to predict the formation of isosulphocyanates.

The question, Whether the replacement of the oxygen in the above-mentioned compounds would lead to the formation of corresponding sulphur derivatives? or, Whether there would be a splitting up into several molecules, accompanied by a molecular re-arrangement? seemed to present a field of considerable interest, and we publish the following preliminary work to reserve the right of future investigation in that direction. The replacement of oxygen by sulphur in organic compounds is dependent on the nature of the oxygen compound. In some compounds, like the aldehydes, the oxygen can be replaced by treatment with hydrogen sulphide; most oxygen compounds, however, are not acted on by that reagent. We are indebted to Kekule[1] for the introduction into organic chemistry of a reagent which possesses the power of replacing oxygen by sulphur in the great majority of oxygen compounds. Thus Kekule showed this to be true with anhydrides, Wislicenus[2] with acetones, Hofmann[3] and Bernthsten[4] with amides.

The following experiments serve to prove that this is also the case with carbimides. Equal weights of phenylisocyanate and finely powdered phosphorus pentasulphide were heated, in a flask with reflux cooler, in an oil-bath at 160°. The disappearance of the sharp cyanate odor is noticeable after heating but a short time, and the reaction is entirely completed on heating the mixture several hours. The product of the reaction was heated with a free flame, as long as a liquid passed over, and the distillate subjected to fractional distillation. The greater part of the distillate passed over from 220°–225°, and a subsequent fractionation gave a liquid boiling between 222°–223°. This oil showed all the properties of phenyl mustard oil. Its formation was also proved by obtaining sulphocarbanilide by its action on aniline, and comparing the sub-

[1] Annalen der Chemie **90**, 311.
[2] Zeitschrift für Chemie, 1869, 354.
[3] Berichte, 1878, 338.
[4] Berichte, 1878, 503.

stance thus obtained with a product formed by the action of aniline on mustard oil,[1] as well as by a sulphur estimation.

0.2508 gram of substance gave 0.2617 gram of $BaSO_4$.

	Theory for $CS(NHC_6H_5)_2$.	Found.
S	14.0	14.3

The yield of phenyl mustard oil obtained from phenylisocyanate by the action of P_2S_5 is almost the theoretical, and the reaction may be expressed as follows:

$$5C_6H_5NCO + P_2S_5 = 5C_6H_5NCS + P_2O_5.$$

The formation of phenylisocyanate by the action of dehydrating agents on phenylurethane led us to expect, inasmuch as phosphorus pentasulphide possesses strong dehydrating properties, the direct formation of phenyl mustard oil by the action of the sulphide on the urethane. The result of our experiment confirmed our anticipation.

Ten grams of phenylurethane and 14 grams of phosphorus pentasulphide were mixed intimately, brought into a retort and heated in an oil bath. The oil which passed over was subjected to a fractional distillation, and consisted largely of a liquid boiling from 220°–225°. In a large measure this liquid was made up of phenyl mustard oil, but it was found impossible to separate it by distillation from a small quantity of ethyl mercaptane formed at the same time. To prove the presence of mustard oil, aniline was added, and the sulphocarbanilide thus obtained was found to be identical in its properties with the ordinary substance. The yield of mustard oil obtained by this method is satisfactory. We believe the method may be developed so as to be used to advantage in the preparation of mustard oils. It is hardly to be doubted that other urethanes would yield the corresponding mustard oils. From the distillate obtained by the action of P_2S_5 on phenylurethane, on standing for several weeks, a crystalline substance separated. This substance contained sulphur, but it is formed in so small a quantity that we were prevented from further examination.

In order to show that the formation of mustard oils from isocyanates is capable of generalisation, we prepared ethylisocyanate, by distilling potassium isocyanate with potassium ethylsulphate, and

[1] The melting point of sulphocarbanilide is given in text-books as 144°, although Bernthsten has, we believe, corrected it to 148°. The melting point of the compound we obtained was 153°, this we found to be correct for sulphocarbanilide prepared from phenyl mustard oil and aniline.

subjected it to the action of P_2S_5. Five grams of ethylisocyanate and five of finely powdered P_2S_5 were heated, in a flask connected with a reversed cooler, until no liquid was noticed to condense in the cooler. The flask was heated as long as a liquid passed over, and the distillate subjected to a fractional distillation. The greater part of the oil passed over at 133°, and agreed perfectly in its other properties with those of ethyl mustard oil. It united with aniline to form ethylphenylsulphurea, melting at 99°.

A sulphur estimation gave the following result:

0.325 gram of $CS\begin{cases} NHC_6H_5 \\ NHC_2H_5 \end{cases}$ gave 0.4246 gram of $BaSO_4$.

	Theory for $C_9H_{12}N_2S$.	Found.
S	17.7	17.9

We have made several experiments in the direction indicated in the beginning of this note, and find that by the action of phosphorus pentasulphide on ethyl isocyanurate, a heavy oil; on methyl isocyanurate, a substance containing sulphur, and finally on potassium isocyanate, a crystalline body containing potassium and sulphur and easily soluble in alcohol, is formed. We hope to describe the results of these, and other similar experiments, in our next note on this subject.

TUFTS COLLEGE, MASS., *Oct.* 11, 1884.

INVESTIGATIONS ON THE SULPHINIDES.

BY IRA REMSEN.

The first representative of the class of compounds known as sulphinides was described by Fahlberg and myself,[1] who obtained it by oxidising ortho-toluene-sulphamide with potassium permanganate. While the isomeric amides of the meta- and para-series are converted by potassium permanganate into carboxyl acids of the formula $C_6H_4{<}\begin{matrix} SO_2NH_2 \\ COOH \end{matrix}$, the product obtained from the

[1] This Journal **1**, 430.

ortho-amide contains the elements of water less than the normal acid. It is an anhydride of ortho-sulphamine-toluic acid, and, in accordance with the methods of representation generally adopted, has one of the three formulas: $C_6H_4\begin{cases}SO_2\\CO\end{cases}>NH$, $C_6H_4<\begin{matrix}SO{=}NH\\CO\end{matrix}>O$, or $C_6H_4\begin{cases}SO_2\\C{=}NH\end{cases}>O$. Although we have no data enabling us to decide positively between these three possibilities, we may for the present use the first and simplest expression. Since benzoic sulphinide was described, other bodies belonging to the same class have been discovered in this laboratory and elsewhere. Among them may be mentioned the following: The sulphinide, $C_6H_3\begin{cases}SO_2NH_2\\SO_2\\CO\end{cases}>NH$, obtained by Fahlberg[1] by oxidising toluene-disulphamide, $C_6H_3\begin{cases}SO_2NH_2\\SO_2NH_2\ (m)\\CH_3\ (p)\end{cases}$; mesitylenic sulphinide, $C_6H_2\begin{cases}SO_2\\CO\\(CH_3)_2\end{cases}>NH$, obtained from mesitylene-sulphamide by Hall and Remsen[2]; isophthalic sulphinide, $C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NH$, described by Remsen and Coale[3] as a product of oxidation of sulphamine-metatoluic acid; terephthalic sulphinide, isomeric with the preceding compound and prepared by Remsen and Hall[4] in the same way from sulphamine-paratoluic acid; and uvitic sulphinide, $C_6H_2\begin{cases}CO_2H\\CO\\SO_2\\CH_3\end{cases}>NH$, obtained by Jacobsen[5] from para-sulphamine-mesitylenic acid.

The fact that ortho-toluene-sulphamide yields a sulphinide, while the corresponding meta- and para-amides do not, suggests, of course, that the ortho-relation of the carboxyl and sulphamine groups is the essential condition for the formation of the sulphinides. This is, further, in accordance with many other similar facts known to us regarding the formation of anhydrides, anhydro-

[1] This Journal **2**, 185. [2] *Ibid.* **2**, 131. [3] *Ibid.* **3**, 209.
[4] *Ibid.* **2**, 58. [5] Annalen der Chemie **206**, 180.

bases, inner anhydrides, &c., and, although independent proof has not been furnished that in every sulphinide the characteristic groups do occupy the ortho-position relatively to each other, there is no reason to doubt that they actually occupy this position.

In a paper[1] on the oxidation of the sulphamides of naphthalene Comstock and Remsen have shown that the α-amide yields a sulphinide while the β-amide does not. As the oxidation of the α-amide can easily be effected and the product obtained in large quantity, the latter has been subjected to a thorough investigation, with the object of throwing as much light as possible upon the chemical character of the sulphinides. In the following paper an account is given of a number of derivatives of phthalic sulphinide, and experiments are described which show that, under some circumstances at least, possibly under all, the formation of salts of this compound is due to the replacement of the hydrogen of the imide group NH. It has hitherto been assumed that when any sulphinide, $R<\begin{matrix}CO\\SO_2\end{matrix}>NH$, yields a salt, the action takes place as represented by the general equation:

$$R<\begin{matrix}CO\\SO_2\end{matrix}>NH + MOH = R<\begin{matrix}COOM\\SO_2NH_2\end{matrix}>.$$

The product has been regarded as a salt of the corresponding sulphamine acid. The experiments to be described lead us, however, to the conclusion that probably the more common action should be represented by the equation:

$$R<\begin{matrix}SO_2\\CO\end{matrix}>NH + MOH = R<\begin{matrix}SO_2\\CO\end{matrix}>NM + H_2O.$$

Other sulphinides are now under investigation in this laboratory with particular reference to the character of their salts and esters, and it is hoped that it will be possible to determine the conditions which lead to the formation of salts in the sense of each of the above equations.

I.—ON PHTHALIC SULPHINIDE.

By H. N. Stokes.

In the preparation of phthalic sulphinide the directions given by Comstock[2] were followed, though a few modifications were found to be advantageous. After some preliminary experiments, the following

[1] This Journal **5**, 106. [2] *Ibid.*

method was used: 40 grams amide and 32 grams potassium hydroxide were dissolved in water, and 180 grams potassium permanganate added in enough water to make the whole volume up to four litres. The oxidation began in the cold, and the solution became hot. It was finished by heating on a water-bath or over a free flame. When all the permanganate was reduced, which usually required from one to three hours, the mixture was filtered, hydrochloric acid added in excess to the filtrate, and the solution concentrated until crystallisation began. It is desirable not to add a large excess of acid at first, but this may safely be done when the crystallisation begins.

On cooling, the liquid was filled with fine needles of the salt, which was considered to be the acid potassium salt of sulphamine-phthalic acid. These were filtered off, boiled with strong alcohol recrystallised from water, again boiled with alcohol, and finally recrystallised from water, with addition of bone black. The object of boiling with alcohol was to remove phthalic acid and unoxidised amide. These were separated by converting the phthalic acid into the sodium salt and evaporating down to a small volume, when the amide crystallised out. In this way a small quantity of each of these substances was obtained. A further quantity of the acid potassium salt was obtained from the mother liquor by concentrating and separating from potassium chloride. Some sulphuric acid was also formed. Although considerable care was taken in working up the mother-liquors, nothing definite was obtained, except a small quantity of sulphophthalic acid which was isolated in the form of the barium salt. It is not certain that the sulphonic acid was formed during the oxidation process, for it was afterwards shown that it may be formed from the sulphamine acid by treatment with hydrochloric acid.

The crude acid salt, after standing for some time under water, was observed to be mixed with large transparent crystals. These were removed, recrystallised, and found to give the reactions of oxalic acid.

As products of the oxidation, therefore, we have chiefly phthalic-sulphinide, obtained in the form of the potassium compound, a little phthalic, sulphuric and oxalic acids, with a small amount of undetermined products.

About 100 grams of pure acid potassium salt were obtained from 500 grams of the amide, which, as used, was not thoroughly

purified. The analyses of the potassium compound gave results like those already reported by Comstock.

0.2561 gram air-dried salt lost 0.0169 gram H_2O at 120°.

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NK + H_2O$.	Found.
H_2O	6.36	6.59

0.2265 gram anhydrous salt gave 0.0745 gram K_2SO_4.

0.2392 gram anhydrous salt gave 0.0776 gram K_2SO_4.

0.2135 gram anhydrous salt gave 0.1879 gram $BaSO_4$.

0.2563 gram anhydrous salt gave 11.9 cc. N at 20°, and 770 mm.

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NK$.	Found.	
K	14.72	14.75	14.54
S	12.08	12.08	...
N	5.28	5.36	...

The salt crystallises finely. It is very difficultly soluble in cold, but readily in hot, water. It is soluble in several hundred parts of boiling 95 per cent. alcohol, from which on cooling it separates in aggregations of small lance-shaped crystals. From water it crystallises according to circumstances. When precipitated by an acid from its solution in an alkali, it forms long needles, or delicate iridescent plates. In the latter form it comes down from its pure solution when rapidly cooled, but, if the clear solution is allowed to cool undisturbed, nothing comes down at first, but a slight jar starts the crystallisation, and then the size of the crystals seems to be limited only by the size of the vessel. Thus it was obtained in bunches of radiating, opaque, lustrous, lance-shaped crystals, some of which were from five to eight centimetres long. These, however, are very brittle, and readily break up into smaller ones. It loses water slowly but completely at 70°, and rapidly at 100°. It does not fuse below 250°, but does fuse at a much higher temperature.

Neutral potassium anhydro-sulphamine-phthalate,

$C_6H_3\begin{cases}SO_2\\CO\\COOK\end{cases}>NK$. The acid salt decomposes alkaline carbonates readily, when slightly warmed with them. One molecular weight of the salt exactly neutralises one molecular weight of alkali, showing that the salt still contains one replaceable hydrogen. The

neutral potassium salt obtained by exact neutralisation with potassium carbonate, may be evaporated to a viscous mass without signs of crystallisation. After long standing, semi-crystalline, very soluble, globular masses made their appearance, probably indicating a slight tendency of the salt to crystallise. The salt is also easily soluble in alcohol. It may be heated to 300°, when it fuses without decomposition.

0.3296 gram dried at 170° gave 0.1878 gram K_2SO_4.

0.2006 gram dried at 300° gave 0.1147 gram K_2SO_4.

	Calculated for $C_6H_3\{SO_2>NK, CO, CO_2K$.			Calculated for $C_6H_3\{SO_2NH_2, CO_2K, CO_2K$.
		Found.		
K	25.74	25.54	25.63	24.20

Potassium-ammonium anhydro-sulphamine-phthalate, $C_6H_3\{SO_2>NK, CO, CO_2NH_4$. This is obtained by neutralising a solution of the acid potassium salt with ammonia. On concentrating, ammonia is given off, and the solution becomes acid. The dissociation takes place but slowly, so that the solution may be evaporated to a syrup, which solidifies, on cooling, to a mass of crystals. The salt was not analysed.

Mono-silver anhydro-sulphamine-phthalate, $C_6H_3\{SO_2>NAg, CO, CO_2H + H_2O$. This is obtained by adding an excess of silver nitrate to a dilute boiling solution of the acid potassium salt. On cooling it crystallises out in fine, long, colorless, flexible needles, which are pure after one recrystallisation. Comstock also prepared this salt, but his statement that it does not lose water on heating is incorrect. It loses one molecule of water below 135°. It is not in the least discolored by light, and may be heated to 200° without decomposition. It is very difficultly soluble in cold, and by no means readily in hot, water. It may be recrystallised unchanged from dilute nitric acid.

0.2474 gram air-dried salt lost 0.0141 gram H_2O at 135°.

0.1837 gram air-dried salt lost 0.0084 gram H_2O at 140°.

	Calculated for $C_6H_3\{SO_2>NAg, CO, CO_2H + H_2O$.		
		Found.	
H_2O	5.11	5.70	5.47

0.2333 gram anhydrous salt gave 0.0758 gram Ag.
0.1753 gram anhydrous salt gave 0.0569 gram Ag.

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NAg$	Found.	
Ag	32.34	32.49	32.46

Neutral silver anhydro-sulphamine-phthalate,

$C_6H_3\begin{cases}SO_2\\CO\\CO_2Ag\end{cases}>Ag + H_2O$. This is obtained as a semi-crystalline white precipitate on adding silver nitrate to a solution of the neutral potassium or potassium-ammonium salt. It is almost insoluble in boiling water. It is easily soluble in a boiling, moderately strong solution of potassium nitrate, from which it is deposited on cooling. Under some circumstances, however, this solution on cooling forms a transparent, moderately firm jelly. With nitric acid it gives the acid silver salt. It is not changed by light. It contains one molecule of water of crystallisation, which it loses below 135°, and even by long boiling under water. It cannot be heated above 165° without decomposing. The analyses do not agree well, as it cannot be purified by recrystallisation.

0.1858 gram air-dried salt lost 0.0069 gram H_2O at 135°.
0.1982 gram air-dried salt lost 0.0078 gram H_2O at 165°.
0.2026 gram air-dried salt lost 0.0079 gram H_2O at 160°.
0.1970 gram air-dried salt lost 0.0076 gram H_2O at 160°.

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\CO_2Ag\end{cases}>NAg + H_2O$.	Found.			
H_2O	3.92	3.71	3.94	3.90	3.86

A portion of salt which had been boiled for a long time under water lost only a fraction of one per cent. of water at 160°.

I. 0.1904 gram anhydrous salt from the neutral potassium salt gave 0.0932 gram Ag.

II. 0.1894 gram anhydrous salt from the neutral potassium salt gave 0.0937 gram Ag.

III. 0.1947 gram anhydrous salt from the potassium ammonium salt gave 0.1251 gram AgCl.

IV. 0.2118 gram anhydrous salt from the potassium ammonium salt gave 0.1362 gram AgCl.

	Calculated for $C_6H_3\{^{SO_2}_{CO}>NAg.$ $_{CO_2Ag}$	Found.			Calculated for $C_6H_3\{^{SO_2NH_2}_{CO_2Ag}$ $_{CO_2Ag}$
		I.	II.		
Ag	48.98	48.95	49.47		47.06
		III.	IV.		
		48.33	48.39		

The low results obtained in the last two analyses may be explained by the fact that the salt used was made from the potassium ammonium salt which had partly dissociated, thus giving a salt mixed with a little of the acid salt.

Neutral lead anhydro-sulphamine-phthalate,

$C_6H_3\{^{SO_2}_{CO}>N>Pb$ $_{COO}$. An acid lead salt could not be prepared. On mixing the acid potassium salt with lead acetate in the proportions of two molecular weights of the former to two of the latter, crystals of the neutral lead salt were obtained, mixed with unchanged potassium salt. The solution on evaporation gave off acetic acid. The same salt was obtained by mixing solutions of the neutral potassium salt and lead acetate.

The neutral lead salt crytallises in short, colorless, concentrically arranged prisms. It is almost insoluble in boiling water, and cannot be recrystallised. It contains one molecule of water of crystallisation, which it loses below 145°.

0.3102 gram air-dried salt lost 0.0137 gram H_2O at 160°.
0.2851 gram air-dried salt lost 0.0127 gram H_2O at 180°.
0.2869 gram air-dried salt lost 0.0115 gram H_2O at 170°.
0.2273 gram air-dried salt lost 0.0091 gram H_2O at 145°.
0.2181 gram air-dried salt lost 0.0102 gram H_2O at 200°.

	Calculated for $C_6H_3\{^{SO_2}_{CO}>N>Pb + H_2O.$ $_{COO}$	Found.				
		I.	II.	III.	IV.	V.
H_2O	4.00	4.42	4.45	4.01	4.00	4.68

0.2965 gram anhydrous salt gave 0.206 gram $PbSO_4$.
0.2724 gram anhydrous salt gave 0.1872 gram $PbSO_4$.
0.2754 gram anhydrous salt gave 0.1874 gram $PbSO_4$.
0.2182 gram anhydrous salt gave 0.1474 gram $PbSO_4$.
0.2079 gram anhydrous salt gave 0.1462 gram $PbSO_4$.

	Calculated for $C_6H_3\{^{SO_2}_{CO}>N>Pb.$ $_{COO}$	Found.				Calculated for $C_6H_3\{^{SO_2NH_2}_{CO_2}>Pb$ $_{CO_2}$
		I.	II.	III.		
Pb	47.92	47.46	46.95	46.48		46.00
		IV.	V.			
		46.15	48.05			

With the exception of the last, the results lie between that required for a normal, and that for an anhydro-compound. The explanation may be that in the first four preparations which were made from acid potassium salt, a small quantity of an acid lead salt may have been contained. This is confirmed by the fact, that the fifth, which was made from neutral potassium salt, has the composition required by the anhydro formula. The formation of an ester, $C_6H_3\begin{cases}SO_2\\CO\\CO_2CH_3\end{cases}>NCH_3$, from the lead salt shows conclusively that it is an anhydro-compound.

Neutral barium salt. The acid potassium salt gives no precipitate with barium chloride, even after boiling or long standing. The neutral barium salt, obtained by boiling finely powdered and suspended barium carbonate with excess of the free acid, is almost insoluble in water. The results of an analysis were not satisfactory. The salt dried at 135° gave the following:

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\COO\end{cases}>N>Ba$.	Found.	Calculated for $C_6H_3\begin{cases}SO_2NH_2\\CO_2\\CO_2\end{cases}>Ba$.
Ba	37.85	36.36	36.05

Although this approaches much more nearly to the normal compound than that of the anhydro-compound, it appears, in view of the results reached in connection with the other salts, more probable that the salt analysed was not pure.

Anhydro-sulphamine-phthalic acid, or phthalic sulphinide, $C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NH + 2H_2O$. The free acid may be obtained by decomposing the acid potassium salt with hot concentrated hydrochloric acid, but better by decomposing a hot solution of the acid silver salt with hydrochloric acid. On concentrating and allowing to cool, the free acid separates out, and may be obtained pure by one re-crystallisation. It is moderately soluble in cold, readily in hot water and in alcohol, but it is almost insoluble in ether. It crystallises from a moderately dilute aqueous solution in the form of short, thick, colorless needles, often concentrically grouped. From a hot concentrated solution it crystallises in spherical tufts of fine needles. When dry it has a pearly lustre. It contains two molecules of water of crystallisation, and loses one at 120°, and the

other at 155°, when its composition agrees with the formula, $C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NH$. The fusing point of the crystallised acid as observed in the capillary tube is not constant, but depends upon the size of the crystals and rapidity of heating. In general it is at about 155°–160°, but is lower when the heating is rapid, and higher when it is very slow. It is accompanied with frothing from escape of water. The anhydride formed by heating for some time at 150°–155° begins to sublime below 200°, but does not fuse even at 240°. If heated much higher, it fuses and sublimes without apparent decomposition.

0.2329 gram air-dried acid lost 0.0165 gram H_2O at 120°, and 0.0152 gram H_2O at 155°.

0.2034 gram air-dried acid lost 0.0144 gram H_2O at 120°, and 0.0134 gram H_2O at 155°.

0.2288 gram air-dried acid gave 0.2034 gram $BaSO_4$.

0.2657 gram air-dried acid gave 11.58 cc. N at 6.3° and 771 mm.

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NH+2H_2O$	Found.	
$1H_2O$	6.84	7.08	7.08
$2H_2O$	13.69	13.61	13.67
S	12.17	12.19	...
N	5.32	5.38	...

That the water lost by heating is water of crystallisation and not of constitution, and that the anhydride is $C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NH$ and not $C_6H_3\begin{cases}CO_2NH_2\\CO\\CO\end{cases}>O$ will be shown farther on.

Mono-methyl anhydro-sulphamine-phthalate, $C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NCH_3$.

Methyl iodide acts on the anhydrous acid silver salt even in the cold, the reaction being accompanied by a considerable evolution of heat. In a closed vessel the reaction is complete after heating half an hour at 100°. The product was extracted with alcohol, in which it is readily soluble, and purified by many recrystallisations from water. Two substances were isolated, the monomethyl ester

and a small quantity of a substance which crystallised from several hundred times its weight of boiling water in the form of delicate colorless curved needles, which fused at 156°. The quantity obtained was not sufficient for analysis, but it was evidently not the dimethyl ester described below, as they differ markedly in crystalline form and fusing point. The other substance proved to be the expected ester. It is readily soluble in cold alcohol, moderately soluble in cold, readily in hot, water. It crystallises in a number of forms. Occasionally it comes out of its solution in alcohol or water (when allowed to evaporate) in the form of long transversely striated prisms; at other times as tufts of delicate white needles one or two centimetres long, but usually as groups of concentric, long, narrow plates. After many recrystallisations it fuses constantly at 186°–187° (uncorrected) or 190.7°–191.7° (corrected). It is markedly volatile much below this temperature. When fused, it solidifies to a vitreous mass on cooling.

0.2045 gram air-dried substance gave 0.1972 gram $BaSO_4$.

0.2226 gram air-dried substance gave 11.7 cc. N at 14.5° and 7.57 mm.

	Calculated for $C_6H_3\begin{cases}SO_2>NCH_3\\CO\\COOH\end{cases}$.	Found.	Calculated for $C_6H_3\begin{cases}SO_2NH_2\\COOH\\COOCH_3\end{cases}$.
S	13.28	13.25	12.36
N	5.81	6.15	5.41

As the analyses of the neutral potassium, silver and lead salts were not decisive as to whether they are to be regarded as normal salts in which the two hydrogen atoms of the carboxyls are replaced by metals, or as compounds in which a carboxyl hydrogen and an imide hydrogen are replaced, it seemed possible that a study of the esters derived from the neutral silver and lead salts would throw some light on this subject, for it was to be assumed that they would more readily admit of purification than the salts themselves.

Dimethyl anhydro-sulphamine-phthalate, $C_6H_3\begin{cases}SO_2\\CO\end{cases}>NCH_3$ $COOCH_3$.

This was prepared in three ways: 1st, from the neutral silver salt; 2d, from the neutral lead salt; 3d, from the monomethyl ester by treating with phosphorus pentachloride and methyl alcohol. The same substance was obtained in all cases.

Anhydrous neutral silver salt was heated with methyl iodide to 100°. The reaction was complete in half an hour. The product

was extracted with boiling alcohol in which it is but slightly soluble. On cooling there separated a mass of fine colorless needles. These were recrystallised from alcohol, and from a large quantity of boiling water, and proved on analysis to be the expected dimethyl ester.

0.1580 gram gave 0.1459 gram $BaSO_4$.
0.2005 gram gave 0.1803 gram $BaSO_4$.
0.1696 gram gave 0.1568 gram $BaSO_4$.
0.2221 gram gave 10.99 cc. N at 21° and 757 mm.

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\end{cases}>NCH_3$ $COOCH_3$.	Found.			Calculated for $C_6H_3\begin{cases}SO_2NH_2\\COOCH_3\end{cases}$ $COOCH_3$.
N	5.49		5.61		5.13
S	12.55	12.66	12.37	12.60	11.72

As every precaution was taken to purify the substance, and the fusing point did not change after many crystallisations, the figures leave no doubt as to the formula to be selected. This ester, as well as the salts from which it was made, is derived from the sulphinide by the replacement of the imide hydrogen and a carboxyl hydrogen. The dimethyl ester fuses at 176° (uncorrected) and 180° (corrected). It is difficultly soluble in cold, and very moderately soluble in hot, methyl and ethyl alcohol. It dissolves in not less than 10,000 parts of cold water, and not less than 500 parts of boiling water. From its hot aqueous or alcoholic solution it crystallises in slender, colorless, brittle needles, often as long as three centimetres. It volatilises perceptibly even at 120°. Heated above its fusing point it readily sublimes without decomposition, forming delicate iridescent plates melting at 176° (uncorrected). The fused mass crystallises in long prisms on cooling.

In making the ester from the neutral lead salt it is necessary to heat with methyl iodide in a sealed tube to 120°. The product is identical with that obtained from the silver salt.

Now, as the neutral silver salt and the neutral lead salt used in making the ester were themselves made from the neutral potassium salt, and, as the ester is thus shown to have the formula $C_6H_3\begin{cases}SO_2\\CO\\CO_2CH_3\end{cases}>NCH_3$ and not $C_6H_3\begin{cases}SO_2NH_2\\CO_2CH_3\\CO_2CH_3\end{cases}$, it appears highly probable that the salts themselves have the formulas already ascribed to them, and deduced from the results obtained in analysing them.

They are constituted according to the formula, $C_6H_3\begin{cases}SO_2\\CO\\CO_2M\end{cases}>NM$

and not $C_6H_3\begin{cases}SO_2NH_2\\CO_2M\\CO_2M.\end{cases}$

When a solution of phthalic sulphinide is neutralised salts of the above order are obtained, at least in the cases studied. From this it follows that in solution phthalic sulphinide retains the anhydride condition, and that the water given off from the crystallised substance is water of crystallisation and not water of constitution. It is correctly represented by the formula,

$C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NH + H_2O$, for plainly if it corresponded to the formula $C_6H_3\begin{cases}SO_2NH_2\\CO_2H\\CO_2H\end{cases}$, the neutral salts would correspond to the second of the above formulas.

It is not at all surprising that the imide hydrogen contained in the sulphinide ring $\begin{matrix}-CO\\-SO_2\end{matrix}>NH$ should have acid properties. Many facts are known which would lead us to expect these properties. In the first place, in many of the primary amides the amide hydrogen may be in part replaced by a metal. Thus, for example, acetamide, $CH_3.CONH_2$, gives the compounds $CH_3.CONHAg$, $(CH_3.CONH)_2Hg$ and $(CH_3.CONH)_2Zn$, and many other examples might be quoted. The sulphamides have the same property. Thus we have from benzene-sulphamide the salt $C_6H_5.SO_2NHAg$, and from α-naphthalene-sulphamide, $\alpha C_{10}H_7.SO_2NHAg$. The replacement of one hydrogen in the amide group by an acid radical gives still more strongly acid properties to the remaining hydrogen atom. Thus in dibenzamide, $\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}>NH$, the imide hydrogen may readily be replaced by sodium[1] by dissolving in caustic soda, and from the sodium salt others may be prepared. A still stronger acid is obtained when the compound has the formula $\begin{matrix}R.SO_2\\R'.CO\end{matrix}>NH$ in which R and R'

[1] Barth and Senhofer, Berichte der deutschen chemischen Gesellschaft **9**, 976.

represent the same or different aromatic radicals. Thus Gerhardt and Chiozza[1] obtained benzoyl-benzene-sulphamide, $\begin{matrix}C_6H_5.CO\\C_6H_5.SO_2\end{matrix}>NH$, and showed that it has acid properties. Other similar compounds have since been made.[2] While the salts of compounds of the general formula $R.SO_2NH_2$ are very unstable, being even decomposed by carbon dioxide,[3] the compounds of the order $\begin{matrix}R.SO_2\\R.CO\end{matrix}>NH$ are strong acids, readily decompose carbonates and form stable salts. The characteristic group of these acids is $\begin{matrix}-SO_2\\-CO\end{matrix}>NH$. Now, in the sulphinides, we have instead of a compound $\begin{matrix}R'.SO_2\\R'.CO\end{matrix}>NH$, one of the formula $R''<\begin{matrix}SO_2\\CO\end{matrix}>NH$. It is difficult to see why a substance of the latter constitution should not be as strong an acid as one of the former, and give salts in which the metal replaces the imide hydrogen. As has been shown above, such is certainly the case with phthalic sulphinide. Only one other undoubted case has previously been described. It is that of mesitylenic sulphinide, of which a silver salt of the formula $C_6H_2\begin{cases}SO_2\\CO\\(CH_3)_2\end{cases}>NAg$ has been described by Remsen and Hall.[4]

Constitution of the Acid Salts.

An interesting question suggests itself regarding the constitution of the acid salts of phthalic sulphinide. Are these salts properly represented by the formula, $C_6H_3\begin{cases}SO_2\\CO\\CO_2M\end{cases}>NH$, or by $C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NM$? In other words, does the metal replace the hydrogen of the carboxyl, or that of the imide group?

The simplest way to decide the question seemed to be to study the action of phosphorus pentachloride and an alcohol on the acid potassium salt.

According to Remsen and Fahlberg[5] benzoic sulphinide is not acted upon by phosphorus pentachloride, even when heated with

[1] Jahresberichte der Chemie, 1856, 503.
[2] Gerhardt and Chiozza, *loc. cit.*; Wolkow, Zeitschrift für Chemie, 1870, 579; 1871, 421.
[3] *Loc. cit.* [4] This Journal **2**, 135. [5] *Ibid.* **1**, 431.

it. The same statement is made[1] regarding the compound $C_6H_3\begin{cases}CO\\SO_2>NH\\SO_2NH_2\end{cases}$. From these observations it seemed reasonable to assume that the sulphinide ring in phthalic sulphinide would show a similar stability, while the carboxyl would almost certainly be attacked. By the successive action of phosphorus pentachloride and methyl alcohol on the anhydrous acid potassium salt, we should then have formed the chloride, $C_6H_3\begin{cases}SO_2\\CO>NH\\COCl\end{cases}$, and the ester $C_6H_3\begin{cases}SO_2\\CO>NH\\COOCH_3\end{cases}$. If the ester thus obtained should prove to be identical with the monomethyl ester above described, which was formed from the acid silver salt, it would follow that in the latter ester, and hence probably in all members of the acid series to which it belongs, the radical or metal replaces the carboxyl hydrogen. If, on the other hand, the esters obtained by the two methods should prove to be isomeric, proof would thus be furnished that the radical or metal replaces the imide hydrogen.

Perfectly anhydrous acid potassium salt was finely mixed with two parts phosphorus pentachloride. The reaction took place rapidly on warming for a short time on the water-bath. An unsuccessful attempt was made to extract the chloride with anhydrous ether. The residue left after distilling off the ether from many extractions was solid, but, after washing with anhydrous ether to remove phosphorus oxychloride, it contained only three per cent. chlorine, while the calculated percentage of chlorine in the chloride is 14.46.

The extraction was effected by heating with phosphorus oxychloride containing a little ether. On cooling, the filtrate deposited small transparent prisms. These were well washed with anhydrous ether, pressed between layers of bibulous paper and placed over sulphuric acid. It was not thought best to recrystallise the substance, and it was analysed directly. It fused at 120°–126°, and contained sulphur, chlorine, nitrogen and phosphorus.

0.1871 gram decomposed by boiling water gave 0.3151 gram AgCl.

0.2835 gram decomposed by boiling water gave 0.0700 gram $Mg_2P_2O_7$.

[1] This Journal **2**, 186.

	Calculated for $C_6H_3\begin{cases}SO_2\\CCl_2\\COCl\end{cases}>N.POCl_2$	Found.
Cl	42.51	41.64
P	7.43	6.88

These results, while not satisfactory, agree more closely with the above than with any other formula. The presence of chlorine in place of the carboxyl oxygen is supported by analogy and by the formation of the trimethyl ester described below. The quantity of material did not suffice for another analysis, and a second attempt to obtain it in the crystalline form failed. The low percentage of chlorine may be explained by its having been decomcomposed slightly by the moisture of the air.

Phosphorus compounds similar to that just described have been obtained by Wallach. Thus he obtained[1] a compound $\begin{matrix}CO_2C_2H_5\\|\\CCl_2.NHPOCl_2\end{matrix}$ by treating oxamethane with phosphorus pentachloride, and in the same way the compound $CHCl_2.CCl_2.N(C_2H_5).POCl_2$ was made from the ethyl-amide of dichloracetic acid, $CHCl_2.CONHC_2H_5$.[2] Generally, it is true the first chlorides of the formula $R.CCl_2.NHR$ lose hydrochloric acid and are converted into products of the formula $R.CCl=NR$,[3] and Gerhardt,[4] Wallach[5] and Wolkow[6] have shown that when phosphorus pentachloride acts upon an amide of the formula $\begin{matrix}R.SO_2\\R.CO\end{matrix}>NH$, a product of the formula $\begin{matrix}R.SO_2\\R.CCl\end{matrix}>N$ is formed.

In view of the above facts it is not surprising that a compound $R''\begin{cases}SO_2\\CO\end{cases}>NH$, such as phthalic sulphinide, should give a compound $R''\begin{cases}SO_2\\CCl_2\end{cases}>N.POCl_2$, rather than $R''\begin{cases}SO_2\\CCl\end{cases}>N$. That the product was not of the latter kind is shown conclusively by the analyses and by the formation of the trimethyl ester.

Trimethyl anhydro-sulphamine-phthalate,

$C_6H_3\begin{cases}SO_2\\C(OCH_3)_2\\COOCH_3\end{cases}>NH$. While it has not proved possible to

[1] Annalen der Chemie **184**, 7. [2] *Ibid.* **214**, 223. [3] *Ibid.* **184**, 33, 79, 88; **214**, 202.
[4] *Ibid.* **108**, 214. [5] *Ibid.* **214**, 210.
[6] Berichte der deutschen chemischen Gesellschaft **5**, 139.

obtain salts of phthalic sulphinide which contain more than two atoms of a univalent metal, it is otherwise with the esters. Three methyl groups have been introduced, and the possibility of introducing a fourth is indicated. The liquid from which the chloride above mentioned had crystallised was mixed with an excess of methyl alcohol. A violent reaction took place, so that the liquid had to be kept cool. The excess of methyl alcohol was distilled off, leaving a syrup which crystallised on cooling. This syrup was dissolved in a little hot water, and the solution on cooling deposited abundant crystals. These were recrystallised several times from water when they had a constant fusing point. They contain no water of crystallisation and fuse without loss of weight, the fused mass forming a vitreous mass on cooling, which does not become crystalline after long standing.

0.2126 gram gave 0.1769 gram $BaSO_4$.

0.2341 gram gave 9.95 cc. N at 19° and 761 mm.

0.2280 gram gave 10.45 cc. N at 23° and 762 mm.

	Calculated for $C_6H_3\begin{cases}SO_2\\C(OCH_3)_2\\CO_2CH_3\end{cases}>NH$.	Found.
S	11.15	11.43
N	4.88	4.89 5.18

These results indicate that the substance is a trimethyl ester, as would be expected from a chloride of the above composition. The ester is easily soluble in cold alcohol, moderately soluble in cold, easily in hot water, from which it crystallises in groups of concentric long slender needles, or more frequently in groups of concentric long narrow plates. In appearance it can scarcely be distinguished from the monomethyl ester. It fuses at 140.5–141.5° (uncorrected); 143.5–144.5° (corrected).

To prove that this ester actually corresponds to the crystallised chloride, a small portion of the latter was treated with methyl alcohol. The product obtained had the same appearance and fused at the same point as the ester analysed.

The formation of the chloride, $C_6H_3\begin{cases}SO_2\\CCl_2\\COCl\end{cases}>NH$, and the ester, $C_6H_3\begin{cases}SO_2\\C(OCH_3)_2\\CO_2CH_3\end{cases}>NH$, is analogous to the formation of phthalyl chloride and the esters of phthalic acid recently described by Graebe.

This chemist has shown[1] that there are two dimethyl esters of phthalic acid, one formed by means of the silver salt and methyl iodide, the other from the chloride and sodium methylate. The former is probably to be represented by the formula $C_6H_4\begin{cases}CO_2CH_3\\CO_2CH_3,\end{cases}$ and the latter by $C_6H_4\begin{cases}CO\\C(OCH_3)_2\end{cases}>O$. Similarly tetrachlorphthalic acid gives two diethyl esters.

The trimethyl ester, $C_6H_3\begin{cases}SO_2\\C(OCH_3)_2\\CO_2CH_3\end{cases}>NH$, contains an imide hydrogen, which by analogy should be replaceable by methyl, thus giving a tetramethyl ester.

A hot solution of the ester was treated gradually with very dilute caustic soda. The solution was heated a few moments, when the slight excess of alkali disappeared. More alkali was added and the heating continued until the reaction became permanently alkaline. It was then precipitated with silver nitrate, the precipitate dried at 160°, and heated with methyl iodide. Instead of the expected tetramethyl ester, nothing was obtained but the dimethyl ester melting at 176°. Hence the alkali had saponified the ester, giving the free acid or the monomethyl ester, either of which treated as above would give the dimethyl ester. Lack of time and material prevented further attempt to obtain the tetramethyl ester.

As the experiments just described failed to accomplish the object for which they were undertaken, that is, the determination of the constitution of the acid salts of phthalic sulphinide, the study of the action of phosphorus pentachloride and methyl alcohol on the monomethyl ester was undertaken with the same object in view.

It has been found that phosphorus pentachloride does not readily act on carboxyl when its hydrogen is replaced by an alcohol radical. Hence we should expect the following results, depending upon the constitution of the monomethyl ester.

I. If it has the constitution, $C_6H_3\begin{cases}SO_2\\CO\\COOCH_3\end{cases}>NH$, we would probably have formed the chloride, $C_6H_3\begin{cases}SO_2\\CCl_2\\COOCH_3\end{cases}>NH$, and the ester,

[1] Berichte der deutschen chemischen Gesellschaft **16**, 860.

$C_6H_3\begin{cases}SO_2\\C(OCH_3)_2>NH\\COOCH_3\end{cases}$, *i. e.* the trimethyl ester above described.

II. If, on the other hand, the monomethyl ester has the constitution $C_6H_3\begin{cases}SO_2>NCH_3\\CO\\CO_2H\end{cases}$, we would have either the products corresponding to the formulas, $C_6H_3\begin{cases}SO_2>NCH_3\\CO\\COCl\end{cases}$ and $C_6H_3\begin{cases}SO_2\\C(OCH_3)_2>NCH_3\\COOCH_3\end{cases}$, or the product $C_6H_3\begin{cases}SO_2>NCH_3\\CO\\COCl\end{cases}$ and $\begin{cases}SO_2>NCH_3\\CO\\COOCH_3\end{cases}$, *i. e.* either a tetramethyl ester or a dimethyl ester identical with that already described, and obtained from the neutral lead and silver salts.

Some of the monomethyl ester was intimately mixed with two parts of phosphorus pentachloride. The reaction took place but slowly even on the water-bath. A small portion of the product gave with water the original ester melting at 186°–187°. This chloride resists the action of water much more strongly than the crystallised chloride above described, and has to be boiled for some time before it is completely decomposed. The remainder of the product was boiled with an excess of methyl alcohol. An ester was thus obtained which after recrystallisation from water fused at 174° (uncorrected), and in every other respect resembled the dimethyl ester $C_6H_3\begin{cases}SO_2>NCH_3\\CO\\CO_2CH_3\end{cases}$. The reaction appeared to be quantitative.

Hence, according to the above considerations, the only possible formula for the monomethyl ester is $C_6H_3\begin{cases}SO_2>NCH_3\\CO\\COOH\end{cases}$, and, since this is derived by simple transformations from the acid potassium salt, it follows that in the acid series it is the imide hydrogen which is replaced by the metal or radical, and that in phthalic sulphinide the imide hydrogen has stronger acid properties than that of the carboxyl.

Finally, perfectly anhydrous phthalic sulphinide was treated successively with phosphorus pentachloride and methyl alcohol

and the same trimethyl ester was obtained as from the acid potassium salt by similar treatment. As this ester has been shown to correspond to the formula $C_6H_3\begin{cases}SO_2\\C(OCH_3)_2>NH\\COOCH_3\end{cases}$, it follows that of the two possible formulas for the free acid, viz. $C_6H_3\begin{cases}SO_2\\CO>NH\\CO_2H\end{cases}$ and $C_6H_3\begin{cases}SO_2NH_2\\CO\\CO>O\end{cases}$, the former is the correct one, for, in case the compounds were constituted according to the second formula, the product obtained would in all probability be a dimethyl ester $C_6H_3\begin{cases}SO_2NH_2\\CO\\C(OCH_3)_2>O\end{cases}$.

It will be observed that when phosphorus pentachloride acts on the free acid or its salts, the sulphinide ring is attacked, but that when it acts on the ester, $C_6H_3\begin{cases}SO_2\\CO>NCH_3\\CO_2H\end{cases}$, the ring remains intact.

α-Sulpho-phthalic Acid.

Phthalic sulphinide is slowly attacked by concentrated hydrochloric acid at 100°, but by heating to 150° it is rapidly and completely changed into sulphophthalic acid. Some of the acid potassium salt was thus treated, and the product evaporated to dryness to expel hydrochloric acid. It was then dissolved in a little hot water. No phthalic acid or phthalic sulphinide separated on cooling. The solution was diluted with a large quantity of water, and boiled with an excess of barium carbonate. The barium salt which separated from the filtrate on cooling was recrytallised from water, and exactly resembled the salt $\left[C_6H_3\begin{cases}SO_3\\CO_2\\CO_2\end{cases}\right]_2Ba_3$ otherwise obtained, and described by Comstock.[1]

Barium α-Sulpho-phthalate, $\left[C_6H_3\begin{cases}SO_3\\CO_2\\CO_2\end{cases}\right]_2Ba_3 + 8\frac{1}{2}H_2O(?)$.

The salt loses part of its water at a low temperature, so that though stable in the air, it cannot be obtained with exactly the same per-

[1] This Journal **5**, 107.

centage of water in any two cases. It loses most of its water at 100°, and about one molecule between this and 250°, but no very concordant results could be obtained. After drying at 100° it is very hygroscopic, and in a few hours will take up nearly as much water as it has lost.

The following analyses were made of a salt crystallised from very dilute solutions, so that the liquid had time to cool considerably before crystallisation began:

0.2688 gram air-dried salt lost 0.0396 gram H_2O at 285°.

0.2070 gram air-dried salt lost 0.0309 gram H_2O at 285°.

	Calculated for $\left[C_6H_3\begin{Bmatrix}SO_3\\CO_2\\CO_2\end{Bmatrix}Ba_2 + 8\frac{1}{2}H_2O\right]$.	Found.	
H_2O	14.57	14.73	14.93

Other preparations crystallised at a higher temperature gave a considerably lower percentage of water.

0.2292 gram salt dried at 285° gave 0.1770 gram $BaSO_4$.

0.1761 gram salt dried at 285° gave 0.1371 gram $BaSO_4$.

	Calculated for $\left[C_6H_3\begin{Bmatrix}SO_3\\CO_2\\CO_2\end{Bmatrix}Ba_2\right]$.	Found.	
Ba	45.83	45.42	45.77

The salt gives a fine green fluorescence when heated with resorcin and sulphuric acid and dissolved in an alkali. No acid salt could be obtained by treating with hydrochloric acid.

Neutral potassium α-sulpho-phthalate, $C_6H_3\begin{cases}SO_3K\\CO_2K\\CO_2K\end{cases}$. This is obtained by treating a hot solution of the barium salt with potassium carbonate. It is extremely soluble in water, and could not be obtained in crystalline form. No crystallised acid salt could be obtained by treating the concentrated solution with hydrochloric acid.

Mono-potassium di-silver α-sulpho-phthalate,

$C_6H_3\begin{cases}SO_3K\\CO_2Ag\\CO_2Ag\end{cases} + 2H_2O$. If a solution of silver nitrate is added to a hot and sufficiently dilute solution of the neutral barium or potassium salt, a clear solution is obtained, which solidifies to a transparent jelly on cooling. One part of salt in several hundred parts of water will form a jelly so firm that the vessel may be inverted without losing the contents.

The neutral potassium salt in moderately concentrated solution gives with silver nitrate a heavy precipitate which is almost insoluble in boiling water, but which dissolves quite readily in a hot moderately dilute solution of potassium nitrate. This solution may also gelatinise, but ordinarily it deposits iridescent scales on cooling. If to a very dilute solution of the potassium salt a solution of silver nitrate is added drop by drop, masses of perfectly transparent jelly are formed, which fall to the bottom or remain hanging from the surface of the liquid or sides of the vessel. In a few minutes these become slightly opaque, and this is seen to be owing to the formation of small scales on the surface. These drop off and are replaced by others, so that in an hour the jelly has become converted into scales. For all these cases the salt formed contains one atom of potassium to two of silver, and two molecules of water of crystallisation. It loses this water at 100°, and is then quite hygroscopic.

0.2063 gram air-dried salt lost 0.0134 gram water at 105°.

0.2008 gram air-dried salt lost 0.0126 gram water at 140°.

	Calculated for $C_6H_3\begin{cases}SO_2K\\CO_2Ag\\CO_2Ag\end{cases}+2H_2O$.	Found.	
$2H_2O$	6.74	6.49	6.27

0.1882 gram anhydrous salt dissolved in nitric acid gave 0.1079 gram AgCl. The filtrate evaporated to dryness gave 0.0343 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}SO_2K\\CO_2Ag\\CO_2Ag\end{cases}$.	Found.
Ag_2	43.37	43.15
K	7.83	8.18

With lead acetate the neutral potassium salt gives a gelatinous precipitate which is difficultly soluble in boiling water, the solution gelatinising imperfectly on cooling. It could not be obtained in crystalline form. It is easily soluble in a hot solution of potassium nitrate, and comes down as an amorphous mass on cooling.

0.2309 gram dried at 175° gave 0.1741 gram $PbSO_4$.

The filtrate gave 0.0195 gram K_2SO_4.

	Calculated for $\left[C_6H_3\begin{cases}SO_2\\CO_2\\CO_2\end{cases}\right]_2Pb_3$.	Found.	Calculated for $C_6H_3\begin{cases}SO_2K\\CO_2\\CO_2\end{cases}>Pb$.
Pb	56.10	51.49	42.33
K	...	3.77	7.98

Hence the salt is probably impure neutral lead salt. The potassium found probably came from the mother liquors which could not be completely removed by washing or pressing.

α-Oxyphthalic Acid.

This acid was first obtained by Miller[1] from α-amidophthalic acid made from the nitrophthalic acid of melting point 212°, and also by oxidising acetyl-α-naphthol with chromic acid.

Jacobsen[2] obtained it from nitro-orthotoluic acid, $C_6H_3\begin{cases}NO_2\\CH_3\ (o)\\CO_2H\ (m)\ (o)\end{cases}$, and from sulpho-orthotoluic acid $C_6H_3\begin{cases}SO_3H\\CH_3\ (o)\\CO_2H\ (m)\ (o)\end{cases}$. Miller[3] called it α-oxyphthalic acid, while Jacobsen called it β-oxyphthalic acid. It is characterised by giving a deep cherry-red color with ferric chloride, while the isomeric acid gives a reddish yellow. If the acid has the formula ascribed to it, it should be obtained by fusing phthalic sulphinide with caustic potash. The acid potassium salt was fused with caustic potash and a little water. The product was acidified and extracted with ether. The substance thus obtained gave an intense cherry-red color with ferric chloride. When dilute it has a more purple tint, but cannot be confused with that produced by salicylic acid. To purify the acid the dry ethereal extract was dissolved in a little ether and precipitated by petroleum benzine. The crystals thus obtained fused at 145°–150° with frothing from escape of water. According to Jacobsen[4] the acid fuses at 200° when rapidly heated, but much lower, with formation of anhydride, when slowly heated. The anhydride melts at 145°–148°. The acid decomposes to a great extent when sublimed, but the sublimate still gives a cherry-red color with ferric chloride.

The *neutral ammonium salt* gives off ammonia when boiled.

Silver α-oxyphthalate, $C_6H_3\begin{cases}OH\\CO_2Ag\\CO_2Ag\end{cases}$. The neutral ammoniacal solution of the acid gives a white precipitate with silver nitrate. This is difficultly soluble in boiling water. When well washed it

[1] Annalen der Chemie **208**, 247.
[2] Berichte der deutschen chemischen Gesellschaft **16**, 1965. [3] *Ibid.* **17**, 552.
[4] *Ibid.* **16**, 1965.

is not sensitive to light and does not decompose very readily on heating, as stated by Miller.[1] It contains no water of crystallisation.

0.2044 gram dried at 110° gave 0.1121 gram Ag.

	Calculated for $C_6H_3(OH)(CO_2Ag)_2$.	Found.
Ag	54.54	54.84

Hence the substance is the *a*-oxyphthalic acid of Miller. Its formation from *a*-nitronaphthalene, on the one hand, and from *a*-naphthalene-sulphonic acid on the other, establishes a line of connection between these two derivatives of naphthalene; and if it be assumed, as seems justifiable, that the formation of the sulphinide is dependent upon the ortho-relation between a sulphamide group and carboxyl, it follows that in *a*-nitronaphthalene the nitro group is situated in the ortho position relatively to one of the carbon atoms common to both benzine residues; and that the constitution of *a*-oxyphthalic acid is represented by the formula

$$C_6H_3\begin{cases}OH\\CO_2H(o)\\COH_2(m)(o).\end{cases}$$

NOTES.

On the Permeability of Silver for Oxygen Gas.

Some years ago Sainte-Claire Deville and Troost showed that hydrogen gas is capable of passing through platinum and iron at a red heat. Recently the latter of these investigators has shown that silver acts in a similar way towards oxygen.

A tube of pure silver of 0.01 m. diameter and with walls 0.001 m. thick was enclosed in a somewhat larger platinum cylinder, and the whole heated in the vapor of boiling cadmium. On exhausting the silver tube with a Sprengel pump, and passing oxygen into the space around it, the gas was found to enter at a rate corresponding to 1.700 lit. per hour for each square meter of surface exposed. On passing air instead of oxygen into the outer chamber, oxygen with only a trace of nitrogen was found in the interior, but the rate of transfusion was diminished nearly one-half. By using a tube of slightly thinner walls, the gas entered much more rapidly. Instead of exhausting the tube, the author found it necessary only to pass slowly through it a stream of some other gas, such as carbon

[1] Annalen der Chemie **208**, 247.

dioxide; although this lessened considerably the rate of transfusion. The oxygen was replaced by other gases, such as carbon dioxide, carbon monoxide, and nitrogen, but they passed through the walls of the tube with extreme slowness. The author states in conclusion that this property of silver may some time be utilised to extract oxygen directly from the atmosphere. For this purpose it would be necessary to expose a large surface by using coils of tubes with thin walls; and to use either an exhaust pump, or a stream of carbon dioxide, which could be absorbed by an alkali, leaving pure oxygen.—(*Compt. Rend. de l'Acad.* **98**, 1427.)

J. R. D.

Recent Methods for the Preparation of Aluminium.

H. A. Gadsden,[1] of London, has patented a process for the manufacture of aluminium, the new feature of which consists in bringing the aluminium chloride and metallic sodium together in the form of vapors. Corundum or bauxite is mixed with about ten per cent. of fluoride of sodium or potassium and the mixture calcined on the hearth of a roasting furnace. After the roasted mass has been pulverised, ten per cent. of charcoal is added, and after thorough mixing and calcining, the mixture is introduced into a retort and heated to a high temperature. A current of chlorine is passed into the retort and the aluminium chloride formed distills over and may be condensed.

For the reduction of the aluminium chloride a furnace is provided in which two earthenware retorts are connected with each other. In one of these aluminium chloride is volatilised, in the other an intimate mixture of sodium carbonate, charcoal and calcium carbonate is heated to a high temperature. The vapors of metallic sodium thus formed pass over into the first retort, the aluminium chloride is decomposed, the metallic aluminium being deposited as a powder in the bottom of the retort, from whence it is easily removed and cast into bars.

W. Weldon[2] proposes to obtain aluminium by fusing cryolite with calcium chloride, or some other non-metallic chloride or sulphide, and to reduce the aluminium chloride or sulphide with metallic manganese.

H. Miwerth[3] mixes ferrosilicon with aluminium fluoride in molecular proportions and heats the mixture to fusion. Double decomposition takes place, silicon fluoride is formed which volatilises, and an alloy of iron and aluminium remains. Aluminium bronze may be obtained directly by fusing the iron aluminium alloy with copper. The aluminium unites with the copper and the iron remains with but a very small quantity of aluminium. Pure aluminium is obtained by heating aluminium chloride with silicon.

E. H. K.

[1] Dingler's Polytechnisches Journal **253**, 426. [2] *Ibid.* **252**, 515. [3] *Ibid.* **252**, 515.

Examination of Fats and Oils.

Hübl[1] describes a systematic method for the detection of fats and oils. It is based upon the fact that nearly all fats are composed of the glycerin ethers of members of three groups of fatty acids. These are the acetic, acrylic and tetrolic acid series. The relative proportion of these acids in any variety of fat or oil is constant within certain limits, and this proportion is different only in different kinds of oils. The members of the three groups of acids, however, exhibit a very different behavior towards chlorine, bromine and iodine, while under ordinary circumstances the acids of the first series are indifferent, those of the second and third series readily unite with definite quantities of the halogens and substitution products of the first series are formed.

If, therefore, it is possible to make a fat unite with a halogen under circumstances which preclude the possibility of substitution, and the amount which enters into the compound be accurately determined, the number thus obtained would be a constant, and would be dependent upon the amount of unsaturated acids present in the fat. An alcoholic solution of iodine and mercuric chloride was found to give better satisfaction than iodine alone. The standard solution was prepared by dissolving 25 grams of iodine and 30 grams of mercuric chloride, each in a half litre of 95 per cent. alcohol and uniting the solutions. After standing from 6–12 hours the strength of the solution was determined by means of a standard sodium hyposulphite solution.

An oil is examined by weighing out from .2 to .8 gram and dissolving in ten cubic centimetres of chloroform; an excess of standard iodine solution is added, and after standing from 1½ to 2 hours the excess of iodine solution determined by means of the sodium hyposulphite solution. By a simple calculation the number of grams of iodine taken up by 100 grams of fat is determined, and this number is a constant for the fat examined. Hübl has determined this constant for a large number of oils and fats. The following are some of his results:

Linseed oil . . .	158.
Walnut oil . . .	143.
Poppyseed oil . . .	136.
Cottonseed oil . . .	106.
Rapeseed oil . . .	100.
Olive oil	82.8
Lard	59.
Oleomargarine . . .	55.3
Palm oil	51.5
Tallow	40.
Butter	31.
Cocoanut oil . . .	8.9
Japanese wax . . .	4.2

[1] Dingler's Polytechnisches Journal **253**, 281.

The method affords a ready means of determining the nature of a fat. In case of a mixture of two known fats or oils the proportion of each present can be readily calculated. Thus let x be the per cent. of one fat and y that of the other, then $x + y = 100$; and if m is the iodine constant for the fat x, and n that of the fat y, and if the number found for the mixture is J; then the quantity of the fat x present in mixture is readily calculated from the equation

$$x = \frac{100(J - n)}{m - n}$$

For example, a commercial olive oil gave on examination 97 as the iodine constant, it was therefore adulterated with a considerable quantity of some other oil. The melting point of the free fatty acids was found to be 30°. This indicated the presence of cottonseed oil, which was confirmed by other tests. Then by substituting in the above formula, the quantity of cottonseed oil present was found to be 60 per cent.

E. H. K.

Combined Carbon in Iron and Steel.

In 1875 Messrs. Schützenberger and Bourgeois studied[1] the properties of the residue obtained by treating cast-iron with copper sulphate, and found that the combustible carbon, which had up to that time been considered pure, is a compound, the composition of which can be expressed by the formula $C_{11}H_6O_3$. Lately Zaboudsky applied himself to the same task and published his results in the Bulletin de la Société chimique de Paris.[2] He examined a specimen of pure Swedish specular iron, containing no phosphorus, sulphur nor graphite, but containing .23 per cent. of silicon and 4.10 per cent. of combined carbon. The metal was finely pulverised and treated with a mixture of sulphate of copper and chloride of sodium. The carbonaceous residue amounted to 5.76 per cent. of the weight of iron taken. This residue was analysed and found to contain 71.60 per cent. of carbon, 26.90 per cent. of water and 1.25 per cent. of siliceous material. The analysis of the carbonaceous portion gave the following result:

Carbon, . .	72.49 per cent.
Water, . .	27.27
Total,	99.72

Its composition may be expressed by the formula $C_{12}H_6O_3$, a result that corresponds very closely with that obtained by Schützenberger and Bourgeois. This compound burns readily in

[1] Comptes Rendus **80**, 1875, p. 911. [2] **41**, 9, p. 424.

the air. Heated to 150° in a sealed tube it does not change. At 200° it loses 6.5 per cent. in weight, and 18.1 per cent. at 325°.

On analysis it now yields:

Carbon, . .	84.51 per cent.
Hydrogen, . .	2.29
Oxygen, . .	13.20

Thus the composition is changed by the loss of water and of a considerable portion of carbon.

If heated in a stream of hydrogen there is in addition to the disengagement of hydrogen and oxygen a partial separation of carbon. Thus the residue, which after losing 24.1 per cent. of its original weight yields on analysis carbon 87.08 per cent., hydrogen 2.27 per cent., and oxygen (by difference) 10.65 per cent., loses upon further heating 33.2 per cent. of its weight, and is now found to contain 96.89 per cent. of carbon and 3.08 per cent. of hydrogen, showing a loss of all its oxygen, 1.2 per cent. of its hydrogen and 7.5 per cent. of its carbon. Upon heating still higher the same tendency to part with carbon rather than hydrogen was noticed, so that it was impracticable to obtain from it pure carbon. It is insoluble in water, alcohol, ether, hydrochloric and sulphuric acids. When treated with nitric acid and warmed it dissolves completely, forming a reddish-brown product having the composition:

Carbon, . .	53.71 per cent.
Hydrogen, . .	2.95 "
Nitrogen, . .	2.90 "
Oxygen, . .	40.44 "

It may be represented by the formula $C_{34}H_{16}(NO_3)O_{19}$. When heated in a tube this compound decomposes, yielding hydrocyanic acid. Chlorine, bromine and iodine also form compounds with this "hydrate of combined carbon," the iodine product having the formula $C_{60}H_{29}IO_{15}$.

Decomposition of the same specimen by chloride of silver yielded a product containing 70.40 per cent. of carbon and 3.59 per cent. of hydrogen. Nor does the decomposition by the battery (according to Weyl's method) yield pure carbon. A specimen of cast-iron examined yielded a residue containing only 71.51 per cent. of carbon.

When cast-iron is treated with mercuric chloride a product is formed containing but 67.72 per cent. of carbon. Hence in determining the combined carbon in iron by Boussingault's method, an error of 32 per cent. may easily occur.

Determination of the combined carbon in steel and cast-iron.—As a result of this investigation Zaboudsky suggests that the following modification of Boussingault's method of determining carbon in steel and cast-iron be made use of:

For the purpose of decomposing the iron or steel, a dry mixture of chloride of copper and chloride of sodium is used. This mixture is obtained by evaporating to dryness a saturated solution of sulphate of copper and chloride of sodium. The metal should be finely pulverised and carefully mixed with this mixture in a mortar. Enough water should then be added to make a paste, and the mass triturated with a pestle, care being taken to keep the mortar cold. The decomposition is effected according to the equation:

$$2\,Cu\,Cl_2 + Fe = Fe\,Cl_2 + 2\,Cu\,Cl.$$

Theoretically 4.8 grams of chloride of copper, or 14 grams of the mixture as prepared above, are required to dissolve 1 gram of iron. Practically, however, 20 grams of the mixture are found to be more convenient.

After half an hour's trituration the pasty mass is raised from the mortar and placed in a beaker, and the mortar washed with ferric chloride (1 pt. Fe_2Cl_6 to 4 pts. water). The glass containing the pasty mass, together with the wash water, is then heated gently, and, after warming, a little hydrochloric acid is added. This operation lasts about forty-five minutes, when the residue can be collected on a filter. This is then dried and burned in the ordinary manner. The loss in weight corresponds to the weight of the hydrated carbon and is *not* the weight of pure carbon, as was formerly supposed.

In order to obtain the true weight of the combined carbon factors must be used. These factors represent the amount of carbon in the hydrate of carbon that has been burned.

In order to determine the mean value of these factors for the various grades of iron Zaboudsky examined a large number of specimens, and gives the following numbers as representing the amount of carbon in the combustible portion of the residue obtained by treating iron and steel in the manner given above:

Pure specular cast-iron (not manganiferous),	.720
Ferro-manganese,	.700
Specular manganiferous cast-iron,	.685
White cast-iron, Pure grey cast-iron,	.710
Steel (cast for cannons and guns, containing about 5 per cent. of carbon),	.660
Hard steel,	.675
Iron,	.690

W. S. B.